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Comparison of Different Approaches for the Calculation of the Integrated Zone and the Cross-over Value in Amplitude Sweep Tests

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Abstract

In soil rheology, the amplitude sweep test (AST) simulates dynamic stresses by means of either increasing shear strain or shear stress and returns information on the viscoelasticity and shear resistance of soils. The dimensionless Integral Z, I_z, is used to compare the microstructural soil stability, based upon the loss factor, $\tan\delta$. Sandy, silty, loamy, and clayey topsoil-samples, equilibrated to defined matric potentials, were subjected to ASTs and pedotransfer functions were derived to test the suitability of soil physical and chemical parameters to estimate the value of I_z. The current approach to the calculation of I_z and of the shear strain and stress values at the cross-over (CO, i.e., where the storage modulus (G') equals the loss modulus (G'')) on the base of the commercial software *RheoPlus* was found to be unprecise due to data simplifications and varying assumptions regarding data interpolation. The deviation of the values at the CO and of I_z of the two calculation methods was evaluated. Considering 132 soil samples, I_z values ranged from 6.8 to 79.4, and the mean value and standard deviation of the difference between the values of I_z as calculated by *RheoPlus* and those calculated as defined by Markgraf et al. (2009) were 0.78 and 1.49, respectively. No difference was found for soil samples with loss factor values smaller than 1 in the complete strain range. A neglectable difference was found for most samples because the loss factor values behind the 'cross-over' were close to 1 and not significantly altered when set to 1. The results underline, that despite the simplifications that were made for the calculations of the rheological parameter, the resulting values of most of the considered samples, do not differ in an unacceptable manner. For the considered soils and matric potentials, the derived pedotransfer functions are applicable to estimate the values of I_z from soil chemical and physical properties such as the soil matric potential, and sand, clay, and soil organic carbon contents.

Keywords: Rheology; Rheometry; Integral Z; AST

Introduction

The mechanical soil stability is controlled by interactions of biological, chemical and physical processes at smaller scales, such as the exudation of biological substances by plant roots and soil microbes, cementing of primary particles by chalk, and the shrink-swell induced development of soil aggregates by water-menisci forces. The aggregate stability, in turn, depends on the aggregate size (Tisdall and Oades, 1982), and is supposed to be stronger in smaller aggregates. Exceeding the soil stability by mechanical loading and shearing results in plastic deformation and the destruction of soil aggregates which define the pore space volumes, results in soil homogenization, and includes the loss of soil functions, such as the water storage and infiltration, and the trafficability of soils (Riggert et al. 2017).

Rheometry is a technique for characterising soil flow behaviour and the soil microstructural stability by applying small strains to small soil volumes. Intensive research has been done concerning the flow behaviour of clay suspensions as affected by pH, particle concentration, temperature (Brandenburg and Lagaly, 1988), organic matter content, salt concentration, ionic strength, type of cation present (Tombácz et al., 1989 and 2004), and clay mineralogy (Au and Leong, 2013). In the last two decades, rheometry was increasingly applied for the investigation of natural soils (Torrance, 1999; Ghezzehei and Or, 2001; Markgraf et al., 2006) and the effect of the aforementioned and of additional physical and chemical soil properties was investigated, e.g., water content, contents of electrolytes (Holthusen et al., 2010; Markgraf and Horn, 2006), organic matter (Khaidapova et al., 2016; Pértile et al., 2018), organic exudates in terms of model substances (Haas et al. 2018a), clay mineralogy (Baumgarten et al., 2013), or particle size distribution (Markgraf and Horn, 2006; Stoppe, 2015), and the applied vertical stress (Holthusen et al., 2017). In amplitude sweep tests (ASTs) increasing shear strains are applied to small soil volumes. The derived values of the storage (G') and loss (G'') moduli represent the soil flow behaviour in terms of an elastic and a plastic deformation component, respectively. The flow behaviour can be distinguished into three phases: (*i*) with small shear strains, the linear viscoelastic range is parameterised, which is characterised by elastic soil deformation. The soil deformation is reversible and no significant soil structural and functional changes are expected (Haas et al., 2016), and (*ii*) with intermediate shear strains, elastic prevails plastic/viscous behaviours, and (*iii*) with shear strains larger than those applied at the cross-over of G' and G'', viscous prevails over elastic soil deformation behaviour, a soil structural breakdown occurs, and the pore system is irreversibly altered resulting in a loss of soil functions (Haas et al., 2016). The Integral z, I_z, was introduced by Markgraf and Horn (2009) as a summarising parameter of the loss factor (i.e., G''/G'; $\tan\delta$) vs. shear strain relationship. The value is calculated by integrating the area between one and the tan δ-values as a function of the applied shear strains with a lower (i.e., shear strain equal to 0.001%) and an upper integration limit (i.e., the shear strain at which the CO occurs) (Fig 2, dotted areas). This dimensionless, semi-quantitative parameter represents the quasi-elasticity of the soil and is used to quantify the stiffness degradation of soils (Batistão et al. 2020; Haas et al. 2018a; Holthusen et al., 2017, 2019, 2020; Khaidapova et al.

2016; Markgraf and Horn 2009; Markgraf et al. 2012; Stoppe and Horn, 2018; Stoppe 2015; Pértile et al., 2016; Pértile et al., 2018), and to identify single stages of thixotropy in allophanic Andosols (Baumgarten et al., 2013).

I_z often is calculated with the rheometer-inherent software *RheoPlus* (*RHEOPLUS/32 V3*.21, Anton Paar, Stuttgart, Germany), following the same calculation steps first conditioned by Markgraf and Horn (2009). However, as found by Haas (2018), Haas et al. (2018a), the measured data are changed within the calculation, and the integration limits are neglected resulting in inaccurate values for the integral Z. Furthermore, an automatic interpolation routine was activated by the software *RheoPlus* for the calculation of the shear strain and stress values at the cross-over of G' and G''. Based on an unknown program-based decision tree, the data were transformed to linear and/or logarithmic scales. Unfortunately, in studies where values of I_z were published, the exact settings of the software have not been reported in detail (e.g., Markgraf and Horn 2009; Holthusen et al. 2017; Heibach et al., 2018; Stoppe and Horn, 2017; 2018). In this way, it can be assumed that all studies followed the same calculation steps first conditioned by Markgraf and Horn (2009). The error nor its magnitude has never been evaluated.

The objectives of this work are to investigated the error and its magnitude for different soils and soil conditions, and to test if pedotransfer functions are suitable to estimate the method-based difference of the absolute values of I_z and of the shear strains at which the cross-over occurs, and to derive pedotransfer functions to estimate the absolute values on the base of easily available soil parameters like the soil texture and the water-filled pore space. We hypothesised that the parameter values are influenced by the calculation methods due to data simplifications and modifications and that the resulting differences and the absolute values can be estimated from physical and chemical soil properties with the developed pedotransfer functions.

Theoretical Background: Amplitude sweep test and data evaluation

Most of the aforementioned studies with natural soils employed a rheometer with a 2.5 cm profiled parallel plate measuring system and conducted an amplitude sweep test (AST) with controlled shear strain. Here, the sample to be tested was enclosed between a fixed lower plate and the upper plate which is moving in an oscillating (i.e., clock- and counter-clockwise) manner with increasing amplitude at a constant frequency of 0.5 Hz. The shear strain applied via the deflection of the upper plate and the torque M needed to achieve the desired strain, is used to calculate the averaged shear stress applied, τ_a, according to Eq. 1 (Mezger, 2012).

$$\tau_a = \frac{2M}{\pi r^3} \qquad \text{(Eq. 1)}$$

with radius, r, of the oscillating upper plate. The shear strain, γ, is implemented in a sinusoidal pattern (Fig. 1a) which changes with time due to the oscillating movement of the upper plate and its increasing amplitude (see Fig. 1b). Depending on the deformation behaviour of the measured substance, the 'immediateness' of its reaction to the deflection of the oscillating upper plate is detected by the rheometer as the phase shift angle, δ, between the applied deformation and the response (i.e., the shear stress wave) of the soil sample. The observed responses (Fig. 1a) include the perfectly elastic response with δ equal to 0°, perfectly viscous behaviour with δ equal to 90°, and the soil typical (Markgraf and Horn, 2006) viscoelastic behaviour with δ larger than 0° and smaller than 90°.

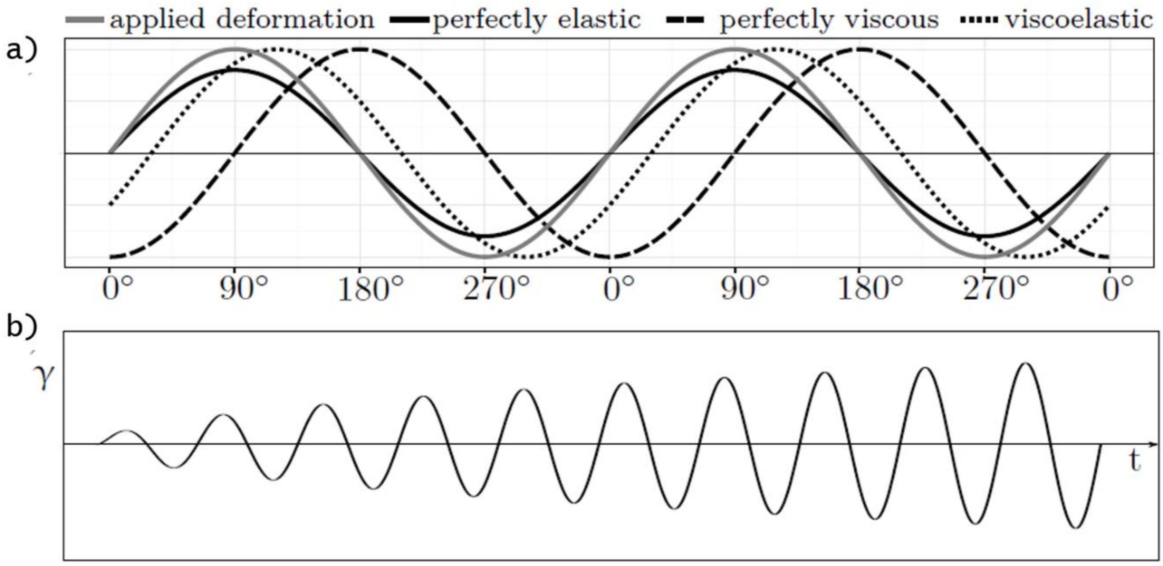

Fig. 1. *a) Flow behaviours as determinable with amplitude sweep tests (ASTs). The sinusoidal pattern of the applied deformation (grey and solid line) and the responses of the sample in case of a perfectly elastic sample (black and solid line, with δ equal to 0°), viscoelastic sample (dotted line, with δ larger than 0° and smaller than 90°), and perfect viscosity (dashed line, δ equal to 90°). Here, a constant amplitude is assumed, while the actual course of the deformation during AST is depicted in b).*

For soil samples and low shear strains, the elastic deformation prevails the plastic deformation with δ smaller than 45°. From given values of γ and the resulting values of τ as well as δ, the storage modulus, G', and loss modulus, G'', can be derived with Eq. 2-3 (Mezger, 2012).

$$G' = \frac{\tau_a}{\gamma}\cos\delta \qquad \text{(Eq. 2)}$$

$$G'' = \frac{\tau_a}{\gamma}\sin\delta \qquad \text{(Eq. 3)}$$

G' is a measure of the elasticity of the soil, representing the energy that is available to reverse the gradual increase of soil deformation, G'' equals the dissipated energy (Mezger, 2012). The relation G''/G' is defined as loss factor, tan δ.

Throughout the further experiments in recent years, I_z was calculated by Haas (2018), Haas et al. (2018a), and Holthusen et al. (2020) directly from raw data using another software than *RheoPlus* and as described by Eq. 4 (Markgraf and Horn, 2009).

$$I_Z = \int_{0.001\%}^{cross-over\ (\%)} (1 - \tan\delta)\, d\gamma \qquad \text{(Eq. 4)}$$

The studies by Haas (2018) and Haas et al. (2018a) noted that the *RheoPlus* software miscalculates the integrated area by setting values of tan δ > 1 to equal to 1, changing the slope of the tan δ vs shear strain relationship (Figs. 2 a-b). In our own data analysis, we have found additionally, that the integration is not limited to the strain value at which the cross-over of G‘ and G“ occurs as right-hand limit as defined by Eq. 4 (Fig. 2a and Table 1), instead data points where tan δ > 1 are included even beyond the cross-over as described by Eq. 5.

$$I_z^+ = \int_{0.001\%}^{100\ (\%)} (1 - \tan\delta) d\gamma \qquad \text{(Eq. 5)}$$

with tan δ larger than 1 set to equal 1.

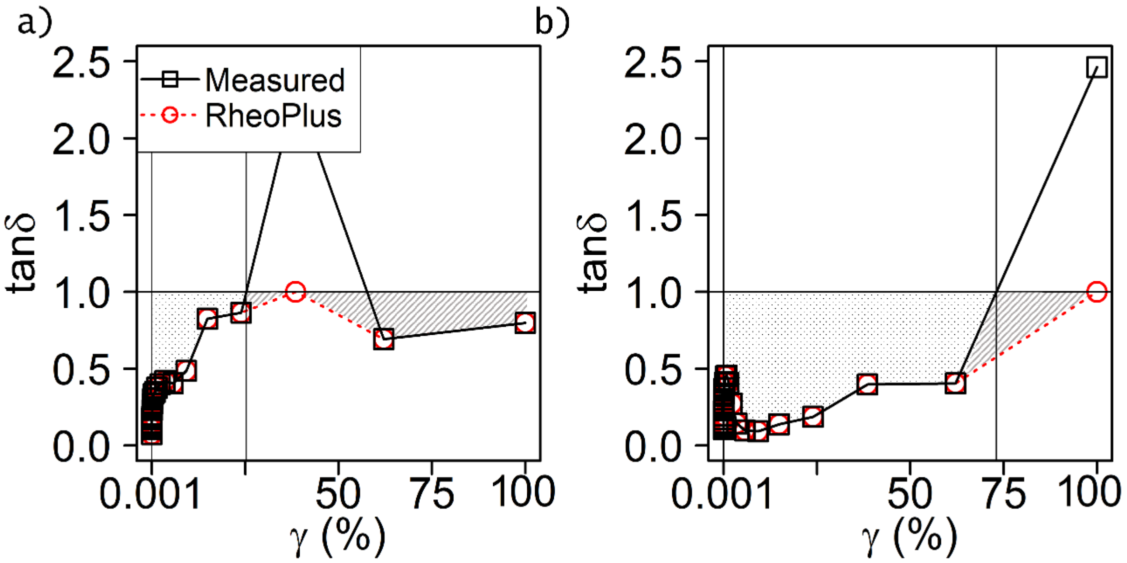

Fig. 2. *Measured loss factors (squares), tan δ, as a function of the shear strain, γ, used to calculate the value of the Integral Z, I_z, and tan δ values as used to calculate the value of the Integral Z, I_z^+, in the RheoPlus software (circles) of a) the sandy soil sample with the maximum deviation, and b) the sample with the second largest deviation between I_z^+ and I_z. The dotted areas represent I_z as defined by Eq. 4 and as calculated with the attached R-script. The dotted and the hatched areas jointly represent I_z^+ as calculated with RheoPlus. See also Table 1 for the detailed calculations for the sample shown in Fig. 2a).*

The shear strain at the cross-over of G’ and G” was then calculated by interpolating measured values in accordance with the detected scaling of the automatic interpolation routine, as described by Eqs. 6-9.

$$G' + a_1 \gamma = G'' + a_2 \gamma \qquad \text{(Eq. 6)}$$

$$\log10(G') + a_1 \log10(\gamma) = \log10(G'') + a_2 \log10(\gamma) \qquad \text{(Eq. 7)}$$

$$\log10(G') + a_1 \gamma = \log10(G'') + a_2 \gamma \qquad \text{(Eq. 8)}$$

$$G' + a_1 \log10(\gamma) = G'' + a_2 \log10(\gamma) \qquad \text{(Eq. 9)}$$

with coefficients a_1, and a_2. The possible interpolation routines alter the values of the shear strain and of G’ at the cross-over (Figs. 3 a) to d)).

Table 1. *Measurement points, MP, shear strain, γ (%), loss factor, $tan\ \delta$, of example data (Fig. 2) and derived values of segments of I_z^+ and I_z by linearly interpolation between the MP. Note: γ and $tan\ \delta$ were rounded to four digits.*

MP	γ	$tan\ \delta$	*n*	$I_z(n)$	$I_z^+(n)$
-	*(%)*			-	
1	0.0001				
2	0.0002				
3	0.0003				
4	0.0004				
5	0.0007				
I1	0.0010	0.1237			
6	0.0011	0.1159	1	0.0001	0.0001
7	0.0017	0.1092	2	0.0006	0.0006
8	0.0028	0.1123	3	0.0009	0.0009
9	0.0045	0.1138	4	0.0015	0.0015
10	0.0073	0.1204	5	0.0024	0.0024
11	0.0117	0.1230	6	0.0039	0.0039
12	0.0189	0.1332	7	0.0062	0.0062
13	0.0304	0.1480	8	0.0099	0.0099
14	0.0489	0.1693	9	0.0156	0.0156
15	0.0788	0.1943	10	0.0244	0.0244
16	0.1269	0.2331	11	0.0378	0.0378
17	0.2043	0.2720	12	0.0579	0.0579
18	0.3290	0.3060	13	0.0887	0.0887
19	0.5297	0.3378	14	0.1361	0.1361
20	0.8529	0.3493	15	0.2122	0.2122
21	1.3730	0.3768	16	0.3313	0.3313
22	2.2110	0.3979	17	0.5134	0.5134
23	3.5610	0.4204	18	0.7976	0.7976
24	5.7340	0.4046	19	1.2766	1.2766
25	9.2350	0.4859	20	1.9422	1.9422
26	14.8700	0.8251	21	1.9413	1.9413
27	23.9500	0.8648	22	1.4079	1.4079
I2	25.3083	1.0000	23	0.0918	-
28	38.5500	2.3180		-	0.9870
29	62.0900	0.6919		-	3.6263
30	100.0000	0.7982		-	9.6652
$\sum$				8.9003	23.0869

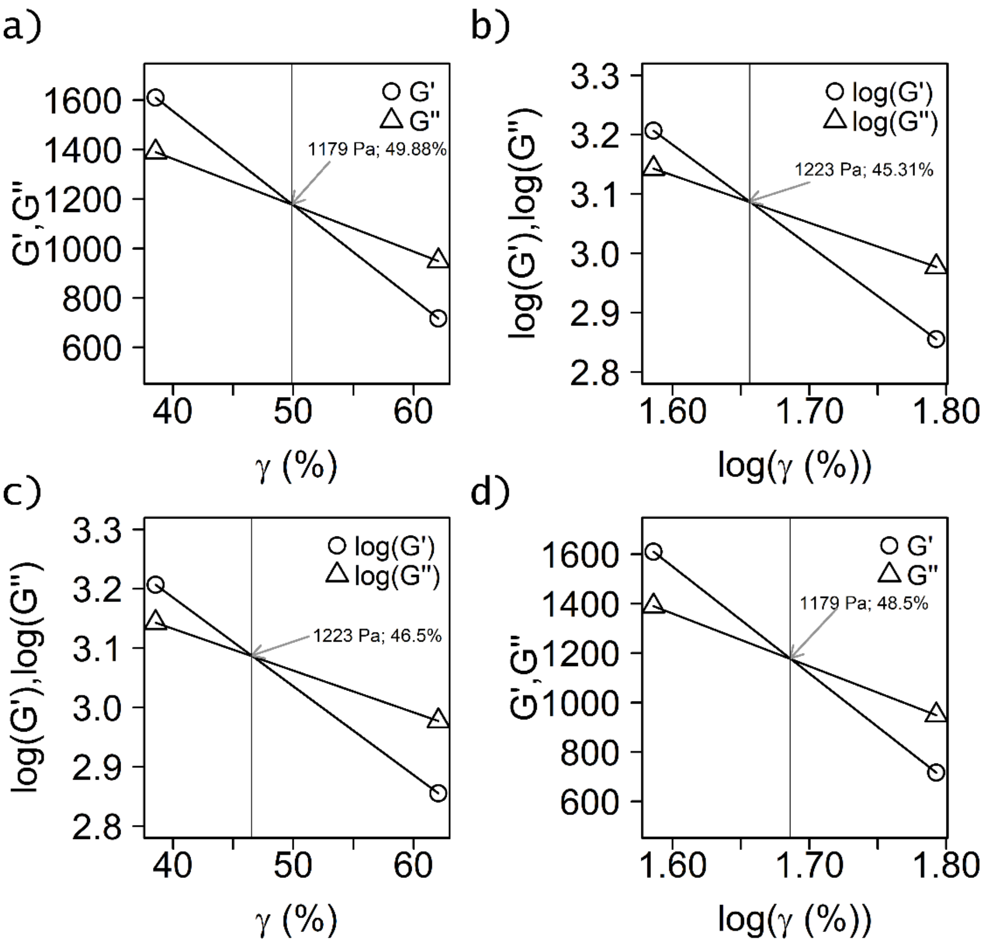

Fig. 3. *Consequence of the automatic interpolation routine for the calculations of the shear strain and stress values at the cross-over (i.e., G' = G"). A program-based decision tree transformed the data to linear (lin) and/or logarithmic (log) scales, and then interpolated the data. The derived values are a function of the scales, namely a) lin-lin, b) log-log, c) log-lin, d) lin-log.*

Material and Methods

2.1 Soil material and sampling sites

Disturbed soil samples were collected from four topsoil horizons, each representing a textural main class (i.e, sand, silt, clay, and loam, see Table 2 for more details). The sandy reference soil (sand) was excavated from the tilled Ap-horizon of an Arenic Podzol (IUSS WRB, 2014) located in Hodenhagen, Germany. On this soil derived from sandy outwash of the Saale glacier, a potassium (K^+) fertilisation trial had been established in 1989. Sampling took place in October 2014 immediately after maize (*Zea mays* L.) harvest. The silty reference soil (silt) was sampled from a loess-derived Haplic Phaeozem (siltic) at the K^+ fertilisation trial experimental site of the Anhalt University of Applied Sciences in Bernburg, Saxony-Anhalt, Germany, which was established in 1993 on loess-derived soil. Samples were excavated after harvest of spring barley (*Hordeum vulgare* L.) in July 2014. The clayey reference soil (clay) was excavated from superficial horizon of an Oxisol, Typic Hapludox

(USDA, 2014) derived from basaltic rocks and located in Vacaria, Rio Grande do Sul (RS), Brazil.

Table 2. *Sand, silt, clay, soil organic carbon (SOC) contents (g kg^{-1} soil^{-1}), pH, of the considered soils.*

Textural class	*Depth*	*Sand*	*Silt*	*Clay*	*SOC*	*pH*	*Location*
	m		*g kg^{-1}*			*-*	
Sand	0 – 0.20	851	99	50	61	4.4	Hodenhagen, Germany
Silt	0 – 0.20	56	719	225	27	7.4	Bernburg, Germany
Loam	0 – 0.20	476	423	101	13	6.1	Cunnersdorf, Germany
Clay	0 – 0.26	71	381	549	34	5.4	Vacaria, Brazil

Sampling took place in July 2013 under cultivated and grazed winter pasture. The loamy reference soil material (loam) was collected from an Eutric Stagnosol derived from sandy loess over Saalean glacial till in Cunnersdorf, Saxony, Germany. Since 1995, the area on the premises of SKW Stickstoffwerke Piesteritz GmbH is subjected to a K^+ fertilisation trial. Sampling took place in August 2016 after the harvest of spring barley (*Hordeum vulgare* L.). For the experimental sites, the plots with K^+ fertilisation, equal to the plant-uptake, were chosen (balanced/optimal fertilisation). Two pits were sampled per sampling site.

2.2 Sample preparation

Air-dried soil was sieved to particle sizes ≤ 2 mm and re-moistened to a gravimetric water content of approximately 10 to 30% depending on clay content and mineralogy. After overnight equilibration, the soil was manually repacked into small cylinders (0.9 cm high and 3.6 cm in diameter) at defined bulk densities, ρ_B, namely, 1.4 Mg m^{-3} for sandy, silty, and loamy soil samples, and 1.1 Mg m^{-3} for clayey samples. Samples were saturated by capillary rise and drained to defined matric potentials, $\Psi_{m,}$ (namely, Ψ_m equal to -0 kPa, -3 kPa, -6 kPa, -15 kPa for sandy, silty and loamy samples, and to Ψ_m equal to -0 kPa, -3 kPa, -6 kPa, -10 kPa for clayey samples) with the help of ceramic suction plates (for Ψ_m equal to -15 kPa) or sand beds (for Ψ_m equal to -0 kPa, -3 kPa, -6 kPa).

For sandy, silty, and loamy soils, ten samples, and for the clayey soils three samples per soil material, and matric potential, i.e., 132 samples in total, were cut horizontally in halves to fit the plate-plate gap of 4 mm using a nylon string, as described in Pértile et al. (2018). While the upper halves were used to determine the volumetric water contents, θ, the lower halves were used for the amplitude sweep test after trimming the diameter of the soil sample laterally to 25 mm. Excessive soil material was removed. The water-filled pore space, *WFPS* (%), was derived from the bulk density, ρ_B (Mg m^{-3}) and the equilibrated water content, θ (Vol.-%), and assuming a specific particle density, ρ_s, of 2.65 Mg m^{-3} (Eq. 10).

$$WFPS\ (\%) = \left(1 - \frac{\rho_B}{\rho_s}\right)^{-1} \cdot \theta \qquad \text{(Eq. 10)}$$

2.3 Amplitude sweep test

Two different modular compact rheometers (both Anton Paar, Stuttgart, Germany) were utilised for the amplitude sweep tests (AST), namely a MCR300 (for sandy, silty and loamy soil samples) and a MCR102 (for clayey soil samples), equipped with identical measurement systems of profiled parallel plates of 2.5 cm in diameter. For an AST, the soil sample is placed on the lower fixed plate of the rheometer while the upper one is moving in an oscillating (i.e., clock- and counter-clockwise) manner with successively increasing amplitudes at a constant frequency of 0.5 Hz, while a constant temperature of 20 °C was maintained by a Peltier unit. As described by Markgraf et al. (2006), the gap between the plates was set to 4 mm, and the strains are applied in a logarithmic ramp (Fig. 2) with 30 steps and increasing shear strains from 10^{-4} to 100%, resulting in a maximum deflection of the upper plate equal to the height of the gap between the plates in both directions at the end of the test.

2.4 Calculation of the I_z value

I_z was calculated with Eq. 4 and by linearly interpolating the $\tan\delta(\mathrm{n})\text{-}\gamma(n)$ relationship for the lower (i.e., $\tan\delta$, at a shear strain, γ_{sp}, equal to 0.001%; Eq. 12) and upper (i.e., $\tan\delta$, at a shear strain, γ_{sp}, equal to 100%; Eq. 12) integration limits.

$$\tan\delta(\gamma_{sp}) = \tan\delta(\mathrm{n}-1) + \left(\frac{\tan\delta(\mathrm{n})-\tan\delta(\mathrm{n}-1)}{\gamma(\mathrm{n})-\gamma(\mathrm{n}-1)}\cdot(\gamma_{sp}-\gamma(\mathrm{n}-1))\right) \qquad \text{(Eq. 11)}$$

$$\gamma(\tan\delta = 1) = (1-\tan\delta(n_{max}))\left(\frac{\tan\delta(n_{max}+1)-\tan\delta(n_{max})}{\gamma(n_{max}+1)-\gamma(n_{max})}\right)^{-1} + \gamma_{x_{max}} \qquad \text{(Eq. 12)}$$

with the measurement point n equal to 1 where $\gamma(n) > \gamma_{sp}$ and $\gamma(n-1) < \gamma_{sp}$ (Fig. 4), and n_{max} equal to the measurement point where $\gamma(n_{max}) < 1$ and $\gamma(n_{max}+1) > 1$.

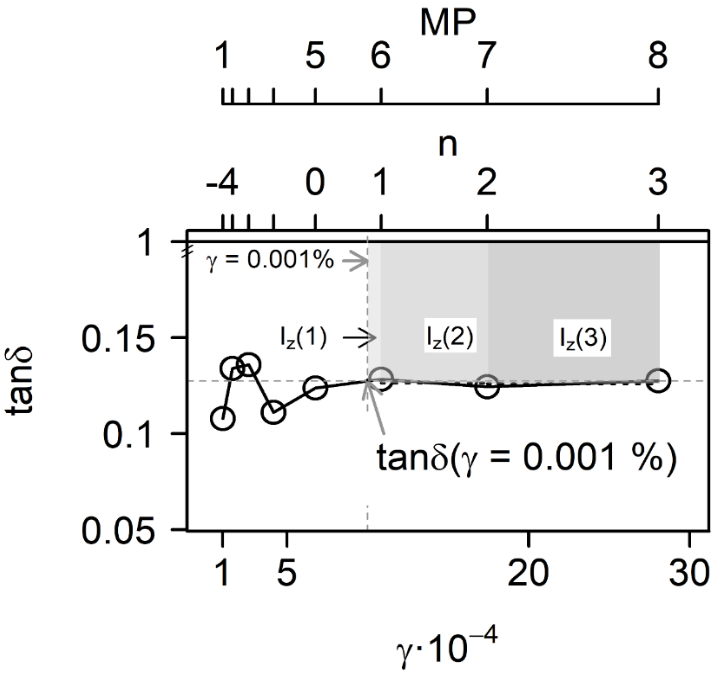

Fig. 4. *Loss factor $\tan\delta$ as a function of the applied shear strain for measurement points (MP) 1 to 8 with the first three sub-segments of I_z (i.e., $I_z(1)$, $I_z(2)$, $I_z(3)$). See Table 1 for values of $I_z(n)$), $\tan\delta$, and γ.*

The values are than integrated as described by Eq. 4. Analogously to Eq. 12, the values of the storage module and shear strain at the cross-over of G' and G'' is calculated.

The R-script attached to this publication (available at https://github.com/CHaasSoil/IntegralZ) can be used to derive the values as described above.

2.5 Statistical analysis

The statistical software R (R Development Team, 2021) was used for data processing and visualisation and for linear analysis of regression. The latter one was performed to test if values of either I_Z or ΔI_Z are predictable from covariates, namely, the water-filled pore space, the matric potential, the contents of sand, silt, clay, soil organic carbon and (volumetric) water, and the pH value. The most insignificant covariates were removed stepwise with the model selections until only covariates with a *p*-value equal to or smaller than 0.05 remained in the models. The values of the shear strain at the cross-over of G' and G'', and I_Z values were derived with the R-script attached to this publication which utilises the *sfsmisc* package (Maechler, 2021).

Results

Values of I_Z (calculated with the presented R script) ranged from 6.8 to 79.4 and most values were similar to those of I_Z^+ (calculated by *RheoPlus*) (as indicated by the 1:1 line in Fig. 5a) except of some values where I_Z^+ was increased as compared to $I_{Z.}$ The values of the shear strain at the cross-over as derived with the new approach were either higher or lower compared to the values derived with *RheoPlus* (Fig. 5b).

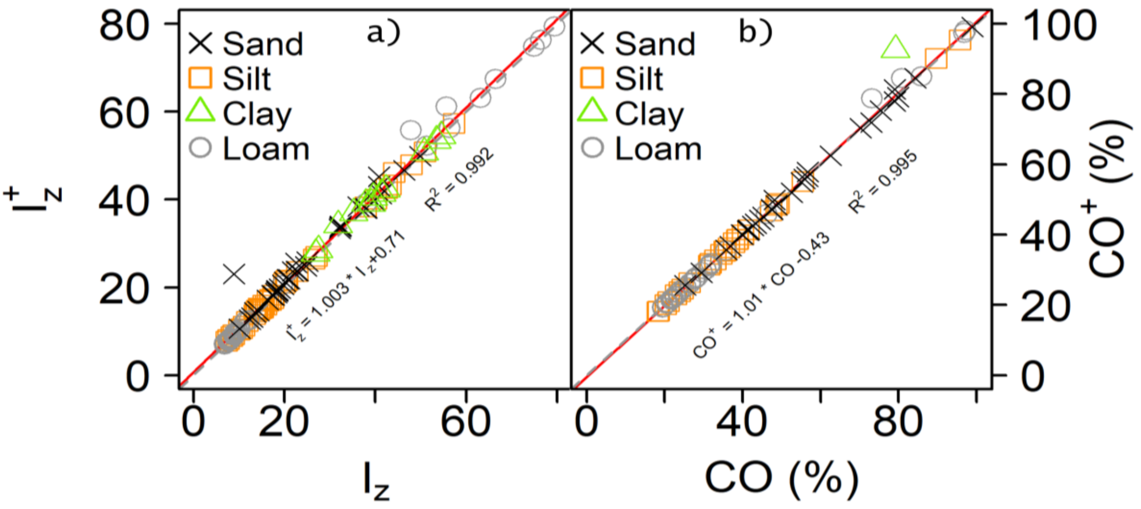

Fig. 5. *a) Integral Z,* I_Z^+*, and b) cross-over value,* CO^+*, for the textural main classes, as derived with RheoPlus as a function of values derived with the new approach with regression lines (red, solid lines), and the line of equality (grey, dashed lines).*

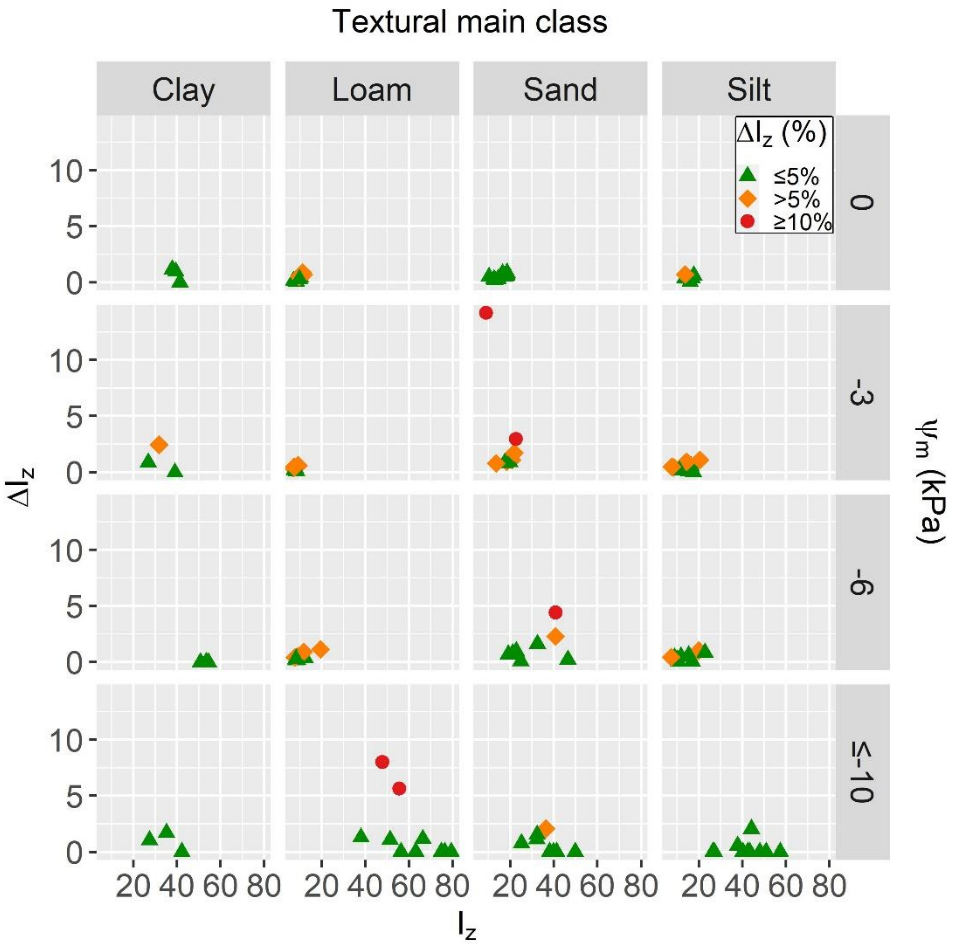

Fig. 6. *Differences between the values of* I_z^+ *and* I_z *(i.e.,* ΔI_z*) as a function of* I_z*, as defined by Eq. 4, for the textural main classes (columns) and soil matric potentials (*Ψ_m *(kPa); rows), for soil samples with a neglectable deviation (i.e., with a relative deviation (i.e.,* ΔI_z *divided by* I_z*) smaller than or equal to 5%; green triangles), with a relative deviation larger than 5 and smaller than 10% (orange rectangles), and for samples with a relative deviation of equal to or larger than 10% (red circles).*

For most of the considered samples, a neglectable difference between $Iz+$ and Iz was found (Fig. 6), because the loss factor values at the 'cross-over' (i.e., where G' equals G'') were close to 1, and not significantly altered when set to 1 (as done with the current calculation procedure).

Values of I_z^+ and I_z did not differ for soil samples with loss factor values smaller than 1 in the complete strain range. Considering all samples, the linear regression (Eq. 13) revealed that the values of I_z^+ were overestimated by around 0.71, as expressed by the intercept, b, independently of I_z, as expressed by a value for a of around 1 (Eq. 13, Fig. 5 a, Table 3).

$$I_z^+ = a \cdot I_z + b \qquad \text{(Eq. 13)}$$

Table 3. *Fitting parameters a and b of the linear regression between I_z^+ and I_z (Eq. 13; $I_z^+ = a \cdot I_z + b$), for defined matric potentials, Ψ_m, and soil materials with adjusted R^2, R^2, and degree of freedom, dF, and p-values.*

Soil	Ψ_m	*a*	*b*	R^2	*dF*	*p-value*
All soils	*≤0*	*1.003*	*0.71*	*0.992*	*143*	*<0.0001*
	0	*1.014*	*0.25*	*0.999*	*31*	*<0.0001*
	-1	*0.915*	*3.77*	*0.989*	*4*	*<0.0001*
	-3	*0.989*	*1.26*	*0.914*	*34*	*<0.0001*
	-6	*1.013*	*0.39*	*0.999*	*32*	*<0.0001*
	≤-10	*1.006*	*0.53*	*0.995*	*68*	*<0.0001*
Sand	*0*	*1.054*	*-0.30*	*0.997*	*7*	*<0.0001*
	-3	*0.365*	*13.87*	*0.098*	*8*	*0.197*
	-6	*1.061*	*-0.51*	*0.986*	*7*	*<0.0001*
	-15	*0.954*	*2.26*	*0.990*	*8*	*<0.0001*
Silt	0	0.983	0.67	0.979	6	*<0.0001*
	-3	1.038	0.01	0.993	8	*<0.0001*
	-6	1.037	-0.06	0.997	7	*<0.0001*
	-15	1.003	0.12	0.995	8	*<0.0001*
Loam	0	1.161	-1.13	0.995	8	*<0.0001*
	-3	1.077	-0.27	0.961	8	*<0.0001*
	-6	1.071	-0.27	0.998	8	*<0.0001*
	-15	0.897	7.96	0.957	8	*<0.0001*
Clay	0	0.658	14.24	0.944	1	0.108
	-1	0.708	10.94	0.933	1	0.117
	-3	0.901	4.08	0.924	1	0.124
	-6	1.001	-0.03	1.000	1	0.002
	-10	0.932	3.30	0.980	1	0.063

Similar values for *a* and *b* were found when the linear regression is done for each textural main class and matric potential separately (Table 3), except for clay samples due to the lower number in repetitions and for sand samples at matric potential of -3 kPa.

The maximum difference of the absolute values of I_z^+ and I_z, ΔI_z, of around 14.2 was found for a sandy soil sample, equilibrated to a matric potential of -3 kPa, and a value of I_z equal to 8.9 (Fig. 6). For this sample, the values of the parameters at the cross-over (i.e., values as calculated with the new approach and as calculated with *RheoPlus*) did not differ. However, *RheoPlus* set values of tan δ > 1 to be equal to 1 and integrated the area within the strain range of 0.001% to 100% (Fig. 2, Table 1), which led to an overestimation of I_z^+ of around 160% as compared to I_z. No differences were found for the clayey soil samples from the Typic Hapludox (except for one soil sample equilibrated to a matric potential of -3 kPa (Fig. 6), and for the silty soil samples from the Haplic Phaeozem equilibrated to a matric potential of -15 kPa. For all textures, except for the clayey soil material, values of I_z increased with more negative matric potentials, except for the clayey soil material in which I_z was larger only at matric potential of -6 kPa. For the loamy and silty soil materials, this increase was most pronounced for samples equilibrated to a matric potential of -15 kPa, while for the sandy soil material, increased values were observed with a matric potential of ≥ -6 kPa.

The model section of linear regression analysis, as described in section 2.5, applied to evaluate the possibility of deriving the value of ΔI_z from soil physical and chemical parameters (Eq. 14), indicated that the value of ΔI_z can be derived just from the sand content, with a p-value of 0.023; R^2 equal to 0.042, and a degree of freedom of 122.

$$\Delta I_Z = 0.00099 \cdot sand\ content(\mathrm{g}\ kg^{-1}) + 0.388 \qquad \text{(Eq. 14)}$$

The results of the model selection for the pedotransfer function, applicable to derive the value of I_Z (Eq. 15), revealed, that I_Z is a function of soil physical and chemical parameters, namely, the soil matric potential, the water-filled pore space (*WFPS*), and the contents of soil organic carbon, clay and sand.

$$I_Z = a \cdot \Psi_m + \mathrm{b} \cdot WFPS + c \cdot SOC + d \cdot clay\ content + e \cdot sand\ content + f \qquad \text{(Eq. 15)}$$

With fitting parameters, *a*, *b*, *c*, *d*, *e*, and intercept *f* (Table 4), the soil matric potential (Ψ_m in kPa), the water filled pore space, *WFPS* (%), the soil organic carbon, SOC, clay, and sand contents (g kg^{-1}). For the considered samples, I_Z increased with decreasing (i.e., more negative) matric potentials and water-filled pore spaces.

Table 4. *Fitting parameters of the model for the prediction of the value of I_Z (Eq. 15), with a, b, c, d, and e, reflecting the influences of the matric potential, the water-filled pore space, and the contents of soil organic carbon, clay and silt, and with intercept f, and, fitting parameters a and b reflecting the influences of the clay and sand contents, and intercept c for the prediction of the shear strain (%) at the cross-over (i.e., where G' equals G''; Eq. 16).*

	Parameter	*Value*	*Std. error*	*t-value*	*p-value*
I_Z	*a*	-3.44	0.40	-8.68	< 0.0001
	b	0.43	0.14	3.11	0.0024
	c	-0.18	0.08	-2.22	0.0280
	d	0.04	0.01	2.92	0.0043
	e	0.03	0.01	4.75	< 0.0001
	f	-37.35	9.70	-3.85	< 0.0002
Cross-over	*a*	0.90	0.16	5.66	< 0.0001
	b	0.23	0.07	3.31	0.0012
	c	-185.77	55.01	-3.38	< 0.0001

with a coefficient of determination, R^2, equal to 0.65, 188 degrees of freedom (dF), and a p-value smaller than 0.0001 for I_Z, and, with R^2 equal to 0.21, 121 dF, and a p-value smaller than 0.0001, for the cross-over value.

Following Table 4, increasing SOM contents decreased the value of I_Z, but I_Z increases with increasing clay and sand contents. This increase is slightly more pronounced for clay as compared to sand (Table 4). The results of the model selection of the pedotransfer function, applicable to derive the value of the shear strain at the cross-over resulted in Eq. 16, based on clay and sand contents:

$$Cross - over\ (\%) = a \cdot \mathrm{clay}\ content + b \cdot sand\ content + c \qquad \text{(Eq. 16)}$$

With fitting parameters, *a*, *b*, and intercept *c*, (Table 4).

Discussion

Calculation errors of values of the Integral Z, I_z, were corrected with the attached R-script. I_z is a summarising parameter and a logarithmic shear strain ramp is applied in the underlying measurement, meaning that the distance between two measurement points increases with increasing shear strains, and therefore, the impact on the value of I_z increases with increasing shear strain. Thus, exact and correct information especially of $\tan\delta$ values at higher strains and of the shear strain at the cross-over of the storage and loss modulus are required. The resulting correlation of I_z and the strain value at the cross-over of the storage and loss moduli, has been pointed out by several studies (e.g., Holthusen et al., 2019; Holthusen et al., 2020; Pértile et al., 2018). That for most measurements no (or a neglectable) difference between the values of the two approaches was found is caused by the soil which remained mostly elastic during the AST and without the occurrence of the cross-over of the storage and loss moduli. Where no cross-over occurs, the previously mentioned errors are avoided and thus, no differences of the two methods are expected. The neglectable differences for the cross-over parameters are possibly caused by varying interpolation routines and rounding errors. Admittedly, the curves of the $\tan\delta$-γ-relationship shown in Fig. 2a represent an extreme and untypical example, and the value of $\tan\delta$ larger than 2 is probably a measuring error, and thus, not very trustworthy. This measurement was not considered in the framework where it had been measured but was identified as measuring error by Heibach (2018). Still, this curve is helpful to impressively demonstrate the calculation errors, which more than doubled the value of the integrated area.

Similar to previous studies (e.g., Stoppe 2015; Stoppe and Horn, 2018), the pedotransfer function indicates that I_z can be derived from soil physical and chemical parameters, reflecting the impact of the soil structure (here, in terms of the soil matric potential and the water-filled pore space), the SOC content, and the soil texture (namely, the sand and clay contents). The stabilising effect of a more negative soil matric potential is well-proven for the considered matric potential range (i.e., 0. to -15 kPa, Pértile et al., 2016) and reference soil materials (except for sandy soil) at the soil core-scale and coincides with a decreasing water-filled pore space. This stabilising mechanism is based on the occurrence of water menisci pulling primary particles together due to the contracting force (caused by the surface tension of the soil pore water), as described by the effective strain Equation (as described e.g., in Horn 2003). However, a change in the shape of the water menisci from concave to convex, e.g., due to shearing forces applied with an AST results in the total loss of the mechanical soil stability by a declining angle of the internal friction.

The mechanical stability of soils is increased by gluing agents like lime, iron oxides, and organic exudates (Haas et al. 2018a) or soil organic matter (SOM) contents in general (Batistão et al., 2020; Pértile et al., 2018). In this study, gluing agents like iron oxides, lime, or biological exudates were not considered, however, the pH value which is indicates the presence of lime, was not identified as factor with significant impact on the value of I_z. The pH values of the considered reference materials were acidic (pH equal to 4.4) to neutral (pH equal to 7.4). While at neutral pH values Ca^{2+} bridges stabilise the primary particles, Al^{3+} contributes to the soil aggregate stability at acidic soil conditions. A decreased soil aggregate stability can be expected within pH values from 5-6.5, due to the absence of both, Ca^{2+} and Al^{3+} bridges.

Contrastingly to the findings of other authors (e.g., Khaidapova et al., 2016), SOM was found to decrease the soil aggregate stability, and consequently, the value of I_z, which indicates a soil loosening effect of SOM at the particle-particle-scale. If hydrophilic, SOM is known to increase the water content at any given matric potential which affects the Chi factor described in the effective stress equation of Bishop (1960). In our experiments, however, defined samples with defined bulk densities were investigated which results in, increasing values for the water-filled pore space with increasing SOM contents. Thus, if shearing forces are applied in the AST, positive water pressures are expected to occur with less intense shearing forces for samples rich in SOM as compared to samples low in SOM, due to an increased ratio of water-filled pores spaces, leading to soil liquification. This generalisation is however critical because SOM is a heterogeneous mixture of organic components containing hydrophilic (C=O) and hydrophobic (C-H) functional groups in varying ratios. The wettability of soils is reduced with increasing ratios of hydrophobic functional groups (Haas et al. 2018b), and a hydrophobicity in soils can persist for several weeks, as shown by Woche et al. (2015).

In previous studies, I_z^+ was used to derive pedotransfer function (Stoppe, 2015) or to identify single stages of thixotropy in allophanic Andosols (Baumgarten et al., 2013). The quality of these studies is not diminished, because the calculation error led to overestimations of the value of I_z but can be easily corrected by applying the attached R-script. However, the calculations by *RheoPlus* resulted in over- and underestimated values of the shear strain at the cross-over, thus, studies focusing on the cross-over value may be more prone to errors. The pedotransfer function for the prediction of the shear strain at the cross-over is not applicable for parameter estimation as indicated by a low value of the coefficient of determination. Following this model, increasing shear stresses at the cross-over of G’ and G’’ can be expected for silty > sandy > clayey soils, as indicated by the slopes of regression coefficients, for any given value of the soil matric potential or, e.g., the WFPS. That solely the sand content can be used to derived to $\Delta I_z$from covariates (i.e., physical and chemical soil parameters) as indicated by the linear model is questionable, since ΔI_z is not only based on mechanical processes but also on calculation errors due to wrong settings in the used software. This is also reflected by the low value of the degree of determination, R^2, (i.e., 0.04), indicating the weaknesses of the model. In conclusion, using a pedotransfer function in order to correct data previously proceeded by the standard *RheoPlus* procedure, might lead to less accurate and representative values than re-calculating the values of I_z and of the cross-over.

Conclusion

Pedotransfer functions were derived to estimate the values of the summarising soil quasi-elasticity parameter, I_z, and of the shear strain at which the cross-over of the loss and storage moduli occurred from soil physical and chemical parameters. Presuming that parameters like the water-filled pore space, the initial matric potential, and SOM, clay, and sand contents are known, the quasi-elasticity can be satisfyingly estimated. The pedotransfer functions indicate that the microstructural soil stability bases on soil hydraulics, soil texture and SOM content.

Results of the two calculation approaches were compared and a maximum deviation between I_z and values calculated by *RheoPlus*, I_z^+, of up to 160% was found for a sandy sample from the tilled A-horizon of an arenic Podzol, equilibrated to a matric potential of -3 kPa. For most of the considered samples, a neglectable method-based difference for I_z was found, because the loss factor values at the ‘cross-over’ (i.e., where G’ equals G’’) were close to 1, and not significantly altered when set to 1 (as done with the current calculation procedure). No method-based difference was found for soil samples with loss factor values smaller than 1 in the complete strain range. For the cross-over values both slightly over- and underestimated values were found with the *RheoPlus* approach and might bias data. The attached script, written in the environment of the open-source software R, can be used to rapidly and correctly calculate I_z, and the cross-over parameters by linearly scaling the storage and loss modulus versus shear strain relationships. In further research, the soil matric potential dynamics and the soil wettability should be considered to better understand the deformation behaviour of soils and the interaction effects of soil mechanics and soil hydraulics.

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Comparative characteristics of Ferric Leptosols

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Abstract

The present study aims to establish the genetic-diagnostic characteristic of Ferric Leptosols and Nudilithic Ferric Leptosols which are formed on rocks with high iron content. Thise soils are spread over hard red sandstones, quartzites and granite gneisses of the ridge parts and the upper (eluvium) parts of the slopes in the hilly part of the northeastern Sofia filed.

The performed diagnostic assessment and characteristics give grounds to include the studied soils in the Bulgarian National Soil Classification at subtype taxonomic level as Ferric Lithozems and Ferric Rankers, and in WRB as Nudilithic Ferric Leptosols and Ferric Leptosols.

Keywords

Ferric Leptosols, Nudilithic Ferric Leptosols, soil diagnostics, soil classifications

Introduction

Modern research in soil science provides an opportunity to improve soil diagnostics and improve the national classification of soils. Objectively, this becomes a fact when defining soil formation processes with certain features and characteristics.

In soil science, the main principle for characterization and evaluation of soils is the genetic-diagnostic approach, which combines the morphology, the structure of the soil profile, the chemical, physico-chemical, physical and other indicators and properties.

On this basis, there were changes in the names of soils in the new bulgarian soil classification (Teoharov et al., 2019) and based on the diagnostic characteristics of WRB (IUSS working group, 2015) new soil units were included. It was found that there are primitive and underdeveloped soils in the country, which have not been studied enough.

The present study aims to establish the genetic-diagnostic characteristic of Nudilithic Ferric Leptosols and Ferric Leptosols formed on rocks with high iron content.

Materials and Methods

In soil-geographical zoning, the group of primitive and underdeveloped soils, in this case Ferric Leptosols and Nudilithic Ferric Leptosols in the Sofia region, is formed in hilly, semi-mountainous areas.

According to the large-scale soil studies of Dishovski (1970) and Yanakiev (1989) in the highest part of the region is located north of the village of Sarantsi with 812.9 m above sea level, occupied by highly eroded Cinnamon forest soils and rocks, shallow, underdeveloped, stony, clayey-sandy, which are incorrectly referred to the zonal type. It is not possible for a soil to be cinnamon (zonal) and at the same time to be defined as underdeveloped (azonal). Geomorphologically, the territory of the studied terrain belongs to the Vitosha mountain-valley part (Galabov, 1982). Soil-forming rock formations are very often complexes of rock individuals of different origins and different lithological varieties. These two features of the formations are especially important for identifying their chemistry and for explaining the chemical features of soils.

Hilly-ridge part - covers the higher part of the hills around the Gorno-Malinska valley and the foot of Stara Planina with a wide distribution of red sandstones, coarse-grained quartzites and their deposited products as deluvial deposits. In this part of the Sofia region the studied soils have the widest distribution.

Field studies were performed on the basis of the profile-genetic approach and the catena method (Mordkovich et al., 1985). According to this methology, the western direction defines as catena any arbitrary part of the slope. The Russian concept allows to consider as catena any micro slope on which there is only one eluvial and one accumulative landscape with transit between them. If the slope has a complex relief, a first-order catenary and several second-order catenaries can be divided on it, each of which must have its own eluvial and accumulative part. Based on these methodological requirements, several second-order rocks were selected, which have inhomogeneous soil-forming rocks and relief in the flat and hilly part, respectively, but are separately characterized by the same soil-forming conditions.

These rocks allow to establish the redistributive functions of relief forms on the conditions and factors of soil formation and their influence on soil formation at different exposures and parent rocks. For the purpose of the development, characteristic areas of soil formation in different ecosystems (pastures and forest ecosystems) are covered. Geomorphology and soil morphology have been studied and described according to the Guidelines for soil description (Jhan et al., 2006). In order to fulfill the objectives of the development, field studies were carried out in the land of the municipality of Gorna Malina, Elin Pelin and it allows them to be differentiated and classified at a lower taxonomic level or defined at the type level.

After an in-depth reconnaissance study and a thorough survey of the terrain, the locations of 3 profiles were selected. The profiles are laid by the method of catena in the northeastern part of the Sofia region, in the land of Gorna Malina.

Profile N. 1 Nudilithic Ferric Leptosols, Profile No: 2 Feric Leptosol, Profile No: 3 Feric Leptosol.

To characterize the type and composition of the soil-forming rocks, data and studies of the Institute of Geology - BAS, and the Sofia University “St. Kliment Ohridski ”

The analysis of soil samples was performed according to the following criteria and methods:

- Mechanical Composition (Kachynski, 1958);
- Soil Color (according to Munsell's Color Scale, Color charts, 1994);

- C: N by calculation (Penkov et al., 1981).
- Composition of humus according to Kononova-Belchikova (Kononova, 1963; Filcheva & Tsadilis, 2002).
- Carbonates by the method of Scheibler (Penkov et al., 1981).
- pH in H_2O and in KCl - potentiometrically with glass electrode.

Results and Discussion

Diagnostic characteristics of the studied soils.

Profile 1 (Nudilithic Ferric Leptosols) with coordinates 42 ° 42.237´N and 023 ° 42.610´ E, with an altitude of 660m in the land of the village of Gorna Malina, Sofia region, in the lower part of a sloping ridge. The soil-forming rock is sandstone, with around bare rock sections and fragments. The vegetation is represented by sparse, most often xerophytic grass formations with a predominance of fescue (Festuca ovina), meadow fescue (Festuca pratensis), jaundice (Genista L.), wild carnation (Dianthus campestris), wild vetch (Vicia sepium L.).), red clover (Trifolium L.), sadina (Andropogon L.), yarrow (Achillea millefolium), windmill (Eryngium campestre L.) and hawthorn (Crataegus monogina L.).

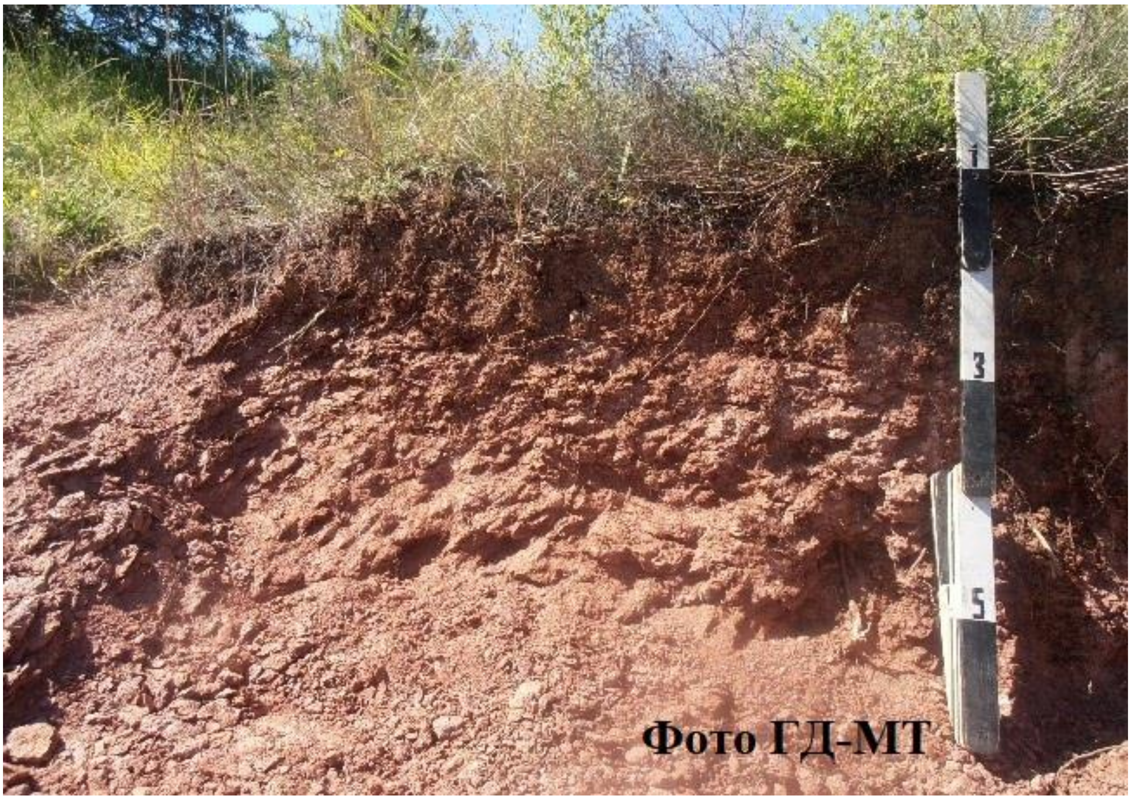

Fig. 1. *Profile 1*

Morphological description:

AC 0-17 cm. Color slightly red 2,5YR 4/2 (dry) and dark reddish brown 2,5YR 3/4 (wet), slightly compacted, unhealthy fine-grained powdery to large structure with aggregate size 1-2 mm (fine up to 60%), with a size of 5-10 mm (large up to 30%) and aggregates> 10 mm (very large 10%), very fine roots 0.5-1 mm in diameter, single fragments of the main scale with rounded sides with a size of 1- 2 cm), signs of high biological activity of insects of various origins, porous, abrupt transition;

CR 17-40 cm. Color slightly red 2,5YR 4/2 (dry) and dark reddish brown 2,5YR 3/4 (wet), semi-weathered rock with an abundance of mica inclusions, massive plate structure with the presence of quartz grains.

Profile № 2 (Ferric Leptosols - Rankers) with coordinates 42 ° 43.082´ N and 023 ° 42.648´ E, with an altitude of 598 m, in the land of the village of Gorna Malina, in the upper part of a ridge with a slope of 6 °. Soil-forming rock is Red Sandstone. The vegetation is represented by xerophytic grass associations with a predominance of sadina (Andropogon L.), thyme (Thymus L.), fescue (Festuca ovina), and less common are Teucrium L., mulberry (Verbascum L.) , puppy (Antirrhium L.), hawthorn (Crataegus L.), dog rose (Rosa canina L.), pubic (Laserpitium L.), oregano (Origanum majorana L.), windmill (Eryngium campestre L.). There are in some places single white pine (Pinus silvestris L.), dogwood (Cornus L.), wild pear (Pirus achras).

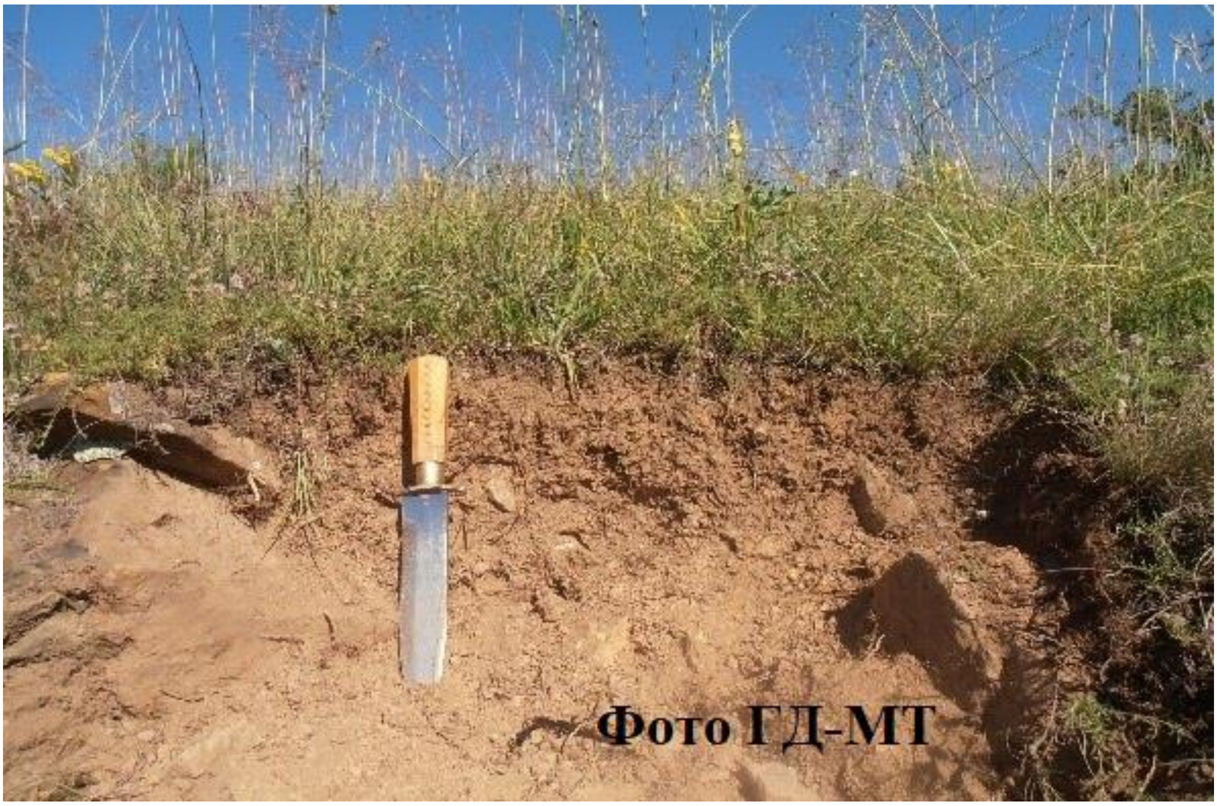

Fig. 2. *Profile 2*

Ah 0-25 cm. Color reddish gray 5YR 5/2 (dry) and brown 7,5YR 4/2 (wet), plenty of pebbles with pointed surfaces 0.5-3 cm in size, fine earth is unstructured, in the dry state strongly dusty, the presence of single larger roots with a diameter of 1-3 mm, a sharp transition;

R 25cm - hard rock.

Profile № 3 (Ferric Leptosols - Rankers)

with coordinates 42 ° 42.269´ N and 23 ° 42.602´ E, with an altitude of 652 m in the land of the village of Gorna Malina, the relief of the area is dissected hilly, the profile is set in the upper part of a slope with 5 ° slope to the north. Soil-forming rock is semi-weathered sandstone. The vegetation is represented by xerophytic grass associations with a predominance of fescue (Festuca ovina), and less common are Teucrium L., wild strawberry (Fragaria vesca L.), thyme (Thymus L.), sorrel (Malus silvestris).), meadow (Poa L.), windmill (Eryngium campestre L.), plantain (Plantago major L.). In the immediate vicinity the terrain is afforested with pine (Pinus silvestris L.) about 30 years old.

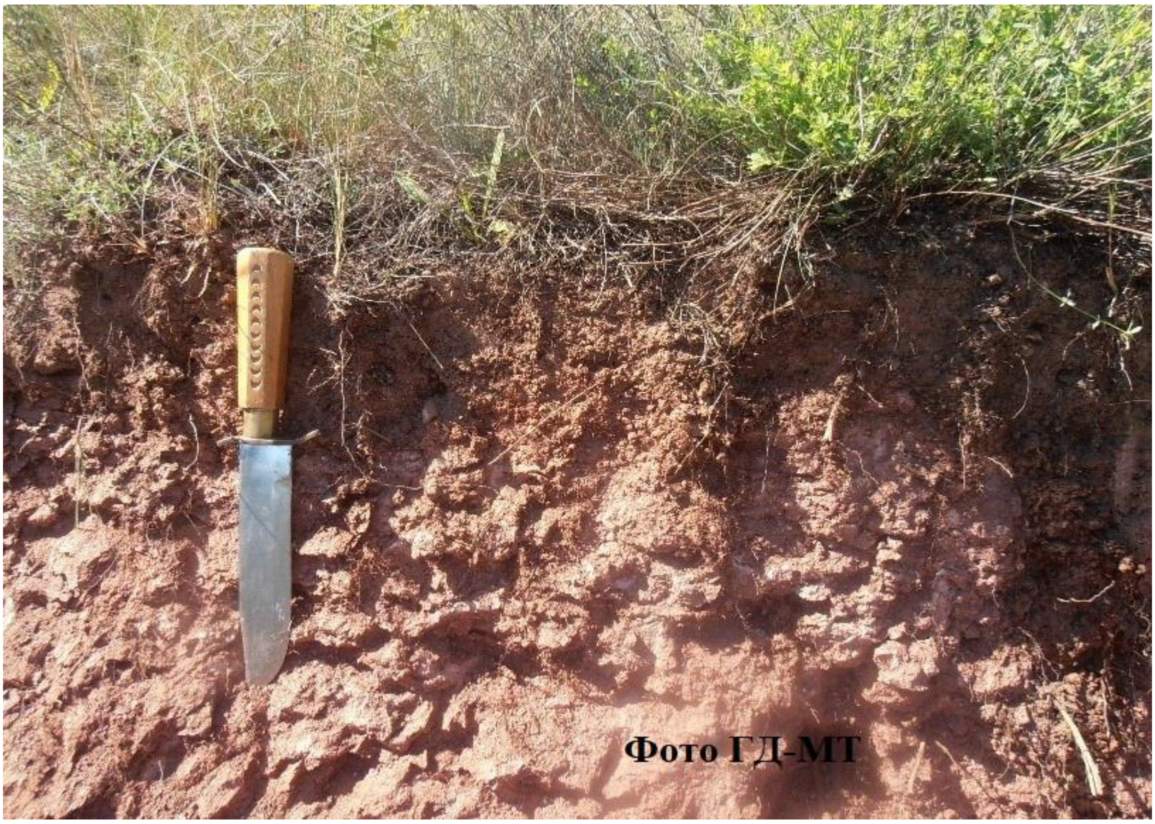

Fig. 3. *Profile 3*

Ah 0-20 cm. Color reddish brown 2,5YR 5/4 (dry) and dark red 2,5YR 3/2 (wet), up to 70% is dominated by highly dusty, unhealthy medium three-shaped, lumpy structure of aggregates with size <5 mm (very fine up to 20 %) and with a diameter of 5-10 mm (fine 10%), single fine roots, the presence of quartz grains, a sharp transition;

CR 20-40 cm. Color light reddish brown 2,5YR 6/4 (dry) and dark reddish brown 2,5YR 3/4 (wet), dense, unhealthy powdery structure up to 50% individual grains, unhealthy chubby structure aggregates <5 mm (very fine) up to 20%) and with a diameter of 5-10 mm (fine up to 30%), individual aggregates are 20-50 mm in size and are highly porous, single fine roots, an abundance of quartz grains.

The morphological description shows that the studied soils are characterized by red chromium in different shades (2,5YR, 4/2, 5/4, 6/4, 5YR 5/2), low power (10-25-30cm), unhealthy structure (powdered), high content of quartz grains, irregularly shaped rock fragments and high porosity. The surface diagnostic horizon is formed on hard or semi-weathered rocks. It is weak, covered with the grass root system and covered with decomposed and semi-decomposed organic residues and with high biological activity. Due to the sloping terrain and the drainage of the soil moisture, the clay formation processes are weak, individual. Annual deposition of organic matter increases the humus content without affecting the pronounced red color of the soil. In general, the soils have an underdeveloped, shallow, skeletal, non-clayey profile, formed on very specific, red-colored soil-forming rocks, which largely determine the lithogenic origin of Fe and iron compounds and their influence on the red color of the clay (mineral) part of the soil. According to Stoykova (2021), this is evidence of the presence of the non-clayey mineral - hematite and the course of rubeification processes, characteristic for the southern Mediterranean type of soil formation. The clay minerals dominate from the illite group. characteristic of the southern Mediterranean type of soil formation. The clay minerals dominate from the illite group. characteristic of the southern Mediterranean type of soil formation. The clay minerals dominate from the illite group.

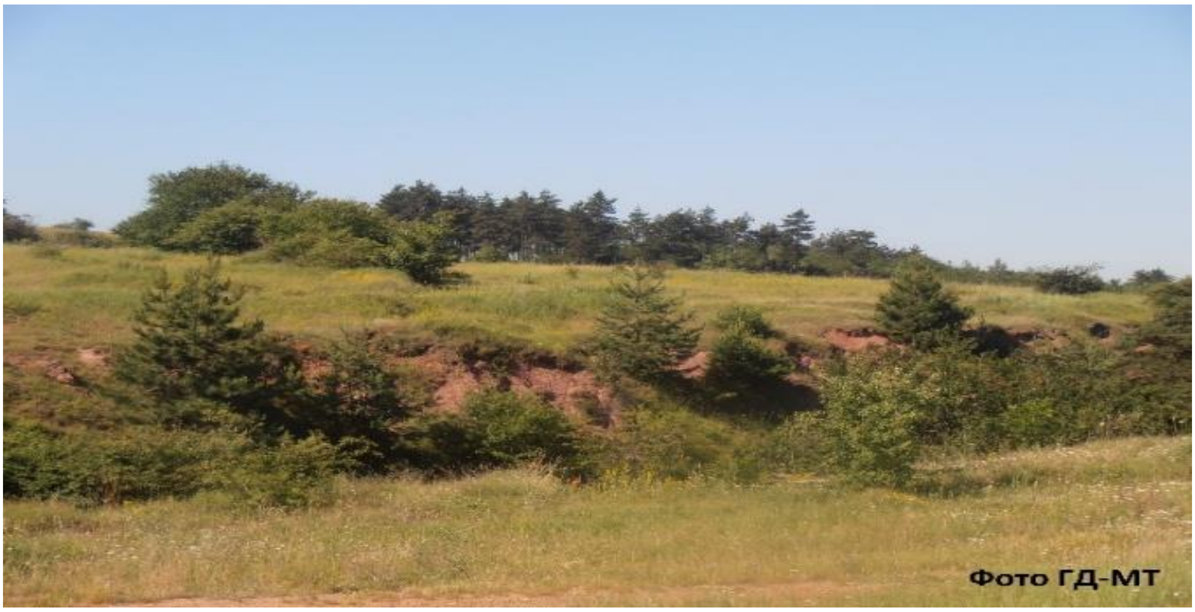

Fig. 4. *Gorna Malina- Open modern red sandstones with shallow weak developed humus-silicate soils (Ferric Leptosol - Rankers) and acid grass formations.*

Table 1. *Diagnostic indicators and characteristics of the studied soils (%).*

Soil Properties	Profile 1		Profile 2		Profile 3	
	AC	CR	Ah	R	Ah	CR
Muncell color	2,5YR 4/2	2,5YR 4/2	5YR 5/2	-	2,5YR 5/4	2,5YR 6/4
Physical clay <0.01 %	14	5.89	21.82	0	15.3	14.6
Clay % <0.001	8.83	2.49	5.62	0	4.8	2.4
SOM (humus) %	3.1	0.67	5.9	0	4.8	1.9
Total Fe %	1.71	1.57	2.87	0	1.32	1.22
pH in H_2O	6.3	6.8	5.1	0	4.9	4.8
Total carbonates in %	0.38	0.52	0.23	0	0	0
Main Clay. Mineralogy	illite		illite		illite	
Additional clay mineralogical identification	montmonilorit-illit	-	illite	-	illite -	-
Primary minerals	quartz, plagioclase, mica	quartz, plagioclase, mica	quartz, mica	- -	-	-
Ratio C / N	12	10	11	0	11	10

The soil texture of the soil reflects the relative content of the different sized partical elements of the fine earth of the soil. This is an important diagnostic indicator for studying the genesis and properties of soils. The clay fraction is a major part of the mechanical composition of all soils, which actively binds organic grains, cations, anions and water molecules in soil aggregates. In table 1 presents the main diagnostic indicators that determine the diagnostic characteristics of soils.

The soil texture usually could be clayey-sandy and sandy-clayey, with a lower content of clay in the Nudilithic Feric Leptosols (up to 14%). The sludge fraction does not exceed 10%. The humus content is about 3% for Leptosols and 5-6% for Rankers (Ferric Leptosols). The content of clay and humus is evidence of the different degree and speed of soil formation processes in different types and their definition as primitive and undeveloped soil. However, the initial initial processes of clay formation (soil formation) determine the low values of the metabolic forms of iron. The steppe nature of the vegetation definitely influences the low values of the C/N ratio and the presence of the type "mull" humus and the porcess of decomposition of the organic matter. According to the pH values and the total carbonate content, these soils are acidic and non-carbonate. Only the soil-forming scale of Profile 1 has a neutral reaction. The increased content of carbonates in AC horizon can be considered as "contamination" of the fragments, but not the presence of carbonates in the clay.

An important diagnostic indicator is the total iron content, which can be defined as high, especially in Rankers (Ferric Leptosols). Apparently its inheritance from the rock and the relatively increased content of silt and clay affects the higher in the surface horizons.

Conclusion

The Ferric Leptosols and Nudilithic Ferric Leptosols are formed on hard red sandstones, quartzites and granite gneisses of the ridge parts and the upper (eluvial) parts of the slopes in the hilly part of the northeastern Sofia valley.

The processes of humus formation (soil formation) mainly involve dilute xerophytic grass communities of degree type, ephemeral species, shrubs, semi-shrubs and single group forest plants, whose organic residues form a "mull" type of humus.

According to the diagnostic characteristic, the studied soils have a primitive (A-CR) or poorly developed AR profile, with shallow, rudimentary, initial, or incompletely developed (weakly deep) surface horizons with thickness 10-25 to 30-40 cm, clay content up to 14 -22%, medium to low humus content.

Iron-weathering soil-forming rocks, high iron content (1.20-2.90%), the formation of red clay and non-clay minerals are evidence of the active processes of ferritization and rubification and the formation of non-clay minerals from the hematite group.

The performed diagnostic assessment and characteristics give grounds to include the studied soils in the Bulgarian soil classification at subtype taxonomic level as Ferric leptosols and Ferric Rankers, and in WRB as Nudilithic Ferric Leptosols and Ferric Leptosols.

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Effect of Soil Organic Matter (SOM) Content on True Particle Density and other Physical Properties of Sudan Savannah Entisols

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Abstract

The study aimed to determine the effect of long-term cultivation and soil organic matter (SOM) content on the particle density (Pd) and other physical properties of an Entisols in Usmanu Danfodiyo University Teachings and Research farm.. Soil samples were taken from six different spots (A, B, C, D, E, and F) at the depth of 0-15 and 15-30 cm. The field experiment was laid in RCB design and replicated three times each at a depth, totalling 36 samples. Purposive random sampling was used at 50 m intervals from one spot to another. The results show that interaction between sampling spots and sampling depths of the soil was significant ($p<0.05$) in terms of total porosity (TP), SOM content, bulk density (Bd), and Pd. Averagely, there was a significant ($p<0.05$) difference between 0-15 cm and 15-30 cm in terms of TP, Bd, and SOM content with the higher values of TP and OM observed in the 0-15 cm depth. The results show that spots near the shelterbelt (C and E) had higher OM, TP, and lower Bd and Pd. In terms of the textural class, differences were also observed among the sampling spots with C and E having sandy loam while the remaining spots had sand texture. Pd was higher in lower OM spots (A, B, D, F). The study revealed that whenever the standard Pd value (2.65 Mg m^{-3}) was used to calculate TP of the soil, particularly spot C and E, it is being overestimated by 2-3%. It is therefore recommended that OM and crop residues should be incorporated and returned immediately after harvesting to help improve the soil properties. When soil is rich in OM, it is recommended that constant value (2.65 Mg m^{-3}) should not be used to calculate its porosity, but rather the actual (measured) Pd of the soil.

Keywords: bulk density, microorganisms, porosity, sandy texture

Introduction

Long-term cultivation tends to lower total porosity because of a decrease in SOM and large peds (Brady & Weil, 2002). The importance of soil organic matter includes an increase of aggregate stability, improving water infiltration and soil aeration, and improves water holding capacity by reducing run-off (Rawls et al., 2004; Kuoe & Joñczyk, 2008). Mikha et al. (2006) reported that addition of OM to the soil can decrease bulk density (Bd) and increase water holding capacity and soil aggregate stability effectively. Carter et al. (2002) noted that the amount of water-stable aggregates was often associated with soil organic carbon (SOC) content, and carbon was often positively related to macro-aggregate stability. The physical decline in OM content is manifested by a decrease in large pore space, a decrease in wet aggregate stability and an increase in Bd (Kuoe & Joñczyk, 2008). Savannah soils are mostly predominated by sandy soils (Jones & Wild, 1975).

Soil physical properties are responsible for the transfer of air, heat, solute, and water through the soil (Nabayi et al., 2019a; Zaibon et al., 2016). Several physical properties can and do change because of management practices adopted on a particular land (Borken & Matzner, 2009). Many soil physical properties degenerate due to continuous cultivation, which renders the soil more susceptible to erosion losses and run-off and less permeable (Sanchez, 1976). Therefore, reliable measurement on a volumetric basis instead of assumption is required for the soil physical properties such as TP, Pd, rate of soil particle sedimentation, thermal conductivity, and heat capacity (Hillel, 1998). The above mentioned are Pd-based parameters, which are vital in modelling and understanding various processes, including air, water, heat flow, and chemical transport through the soil. Such importance of Pd in many applications necessitates an accurate measurement of this soil physical property.

Pd is defined as the density of the soil particles collectively which is one of the basic physical properties of soils (Ruehlmann, 2020). Mathematically it is expressed as the ratio of the soil particles' total mass to their total volume, excluding the pore spaces between particles (Brady, 1990). Soil minerals weigh much more per unit volume than OM (Rawls et al., 2004). Soils with higher OM content had lower Pd than soil similar in textures with low OM (Creswell & Hamilton, 2002; Ruehlmann & Körschens, 2020). Soil Pd generally increases with soil depth because of the concurrent decreases in OM (London, 1991). Pd differs from the type of soil mineral present, as well as the amount of OM. The Pd of most mineral soils is assumed to be 2.65 Mg m^{-3}, but when appreciable amount of magnetite and heavy minerals are present, the soil Pd is greater than 2.65 Mg m^{-3} (Brady & Weil, 2002).

Soils formed in volcanic parent materials such as ash generally had Pd less than 2.65 Mg m^{-3} (Blanco-conqui et al., 2006). London (1991) stated that the actual values of Pd depend upon the mineralogical and chemical composition and degree of hydration of the particles. Zero tillage practice decreased soil Pd compared to mouldboard ploughing because of an increase in SOM (Blanco-conqui et al., 2006). The authors (Blanco-conqui et al., 2006) reported that under these circumstances, if the standard value of Pd is used to calculate TP of the soil, then it is overestimated by 12%. Therefore, they concluded that while a Pd of 2.65 Mg m^{-3} can be accurate for some soils, differences in the compositions of solids, such as an increased SOC concentration, can considerably lower the Pd value since OM fraction is an essential component of soil solid.

Cropping system and tillage influence the Pd significantly, and most importantly, the changes in SOC concentration resulting from these management systems primarily modify the Pd of the soil (Singh et al., 1994). Meanwhile, the conversion of traditional tillage to reduced and zero tillage systems increases soil organic carbon pools (Allmaras et al., 2004; Lal, 2004; Hooker et al., 2005; Nabayi et al., 2019b). The Pd is not, however, routinely measured during soil characterization because it is considered to be a constant value of 2.65 Mg $m^{-3,}$ which ranged between 2.60 and 2.70 Mg m^{-3} of the most quartz-dominated soils (Blanco-conqui et al., 2006). The lack of Pd measurement in many soil studies could relate to the rather laborious measurement procedure (Blake & Hartge, 1986). However, OM is one of the important soil parameters that change Pd (Schjønning et al., 2017). The soil management practices put in place can change the soil densities easily (Adams, 1973; Singh et al., 1994). Soil physical properties such as porosity, Bd and hydraulic conductivity are Pd dependent, hence the need for Pd to be measured as a routine soil properties measurement to prevent over and or underestimation of these properties. Soils that are subjected to tillage, and soils that are receiving organic amendments year in year out are particularly susceptible to change in Pd (Nabayi et al., 2019c). The effects of soil organic carbon increases on Pd have not been well documented, and the general assumption is that changes in Pd are negligible (Blanco-conqui et al., 2006; Ruehlmann & Körschens, 2020; Schjønning et al., 2017). The objective of this research was to determine the effect of long-term cultivation and SOM content on true Pd and other physical properties of Usmanu Danfodiyo University teachings and research dryland farm, Sokoto, Nigeria.

Materials and Methods

Experimental site

The study location was Usmanu Danfodiyo University teachings and research dryland farm, Sokoto, Nigeria. The farm is located within the university premises near Dundaye district, in Wamakko Local Government, Sokoto state on latitude 13^{o} 02^{1} N and longitude 5^{o} 02^{1} E. The soils of the study area were predominantly sandy and had low OM content. The study site falls within the Sudan savannah agroecological zone, which comprises of scattered trees and sparse vegetation. The dominant crops being cultivated on the farm for an extended period are cereals and legumes. The mean annual rainfall ranges between 500-700 mm, and it rains between June and October. Also, the mean annual temperature is greatly variable, ranging from 15 ^{O}C to 40 ^{O}C (SERC, 2010).

Treatments, Experimental Design, Samples Collection and Preparation

The sampling spots (A, B, C, D, E, and F) and sampling depths (0-15 and 15-30 cm) were considered as the first and second factor respectively, which were replicated in triplicate each and arranged in a Randomized Complete Block (RCB) design in a factorial arrangement. These consisted of twelve (12) soil samples from the two (2) depths, which are 0-15 cm and 15-30 cm, respectively replicated three (3) times, making a total of thirty-six (36) soil samples. A purposive random sampling technique was used in selecting the spots at 50 m intervals. The soil samples were taken using auger and cores (5 x 5 cm) which were labelled and taken to the laboratory, air dried, grounded and sieved (< 2 mm) then stored in clean bottle before analysis. Samples for the determination of bulk density were left undisturbed in the core samplers which were oven-dried at 105 ^{O}C for 24 hours.

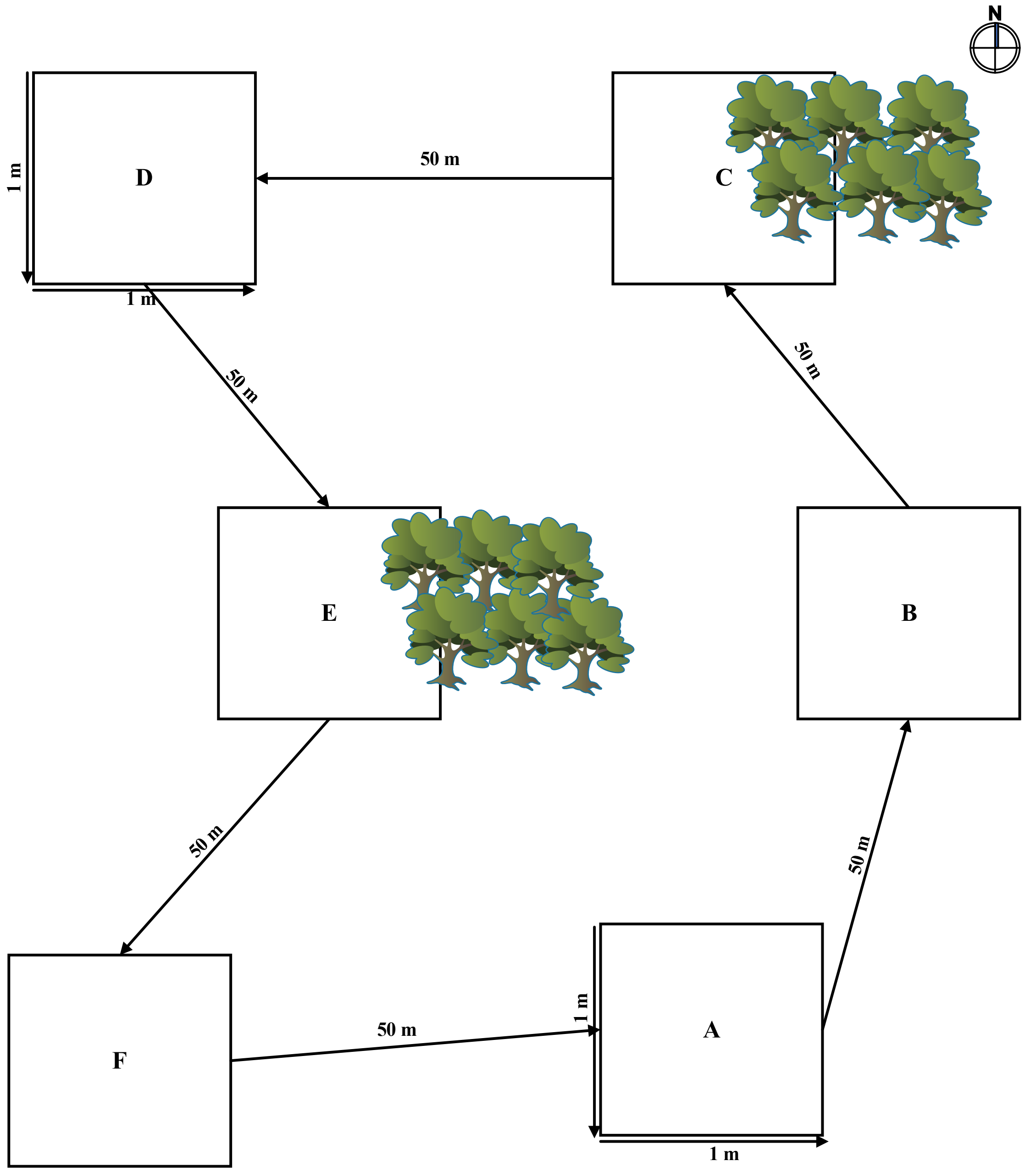

Figure 1: *Field layout and sampling spots*

Determination of Physical Properties

Particle size was determined using the Bouyoucos hydrometer method; where sodium hexametaphosphate (Calgon) was used as a dispersant agent (Gee & Bauder, 1986). The USDA textural triangle was used to determine the textural class of the soil samples.

Particle density was determined using the Pycnometer bottle method (Heiskanen, 1992) from the two measured quantities, namely; a mass of the samples and its volume. The mass was determined by the mass and density of water displaced by the sample.

$$\text{Particle density (Dp) (Mg m}^{-3}\text{)} = \frac{\text{Mass of Soil solid (Ms)}}{\text{Volume occupied by the soil solid (Vs)}} \ldots\ldots\ldots(1)$$

Bulk density was measured using the core method, where undisturbed samples were taken in a core of a constant and known volume (Blake & Hartge, 1986). Bulk density of the samples was calculated from the ratio of the oven-dried mass at 105 ^{O}C for 24 hours to the field volume of the soil as given by the volume of the core sampler as described by Blake and Hartge (1986).

$$\text{Bulk density } (Mg\ m^{-3}) = \frac{Weight\ of\ ovendried\ soil\ sample\ at\ 105^{o}C}{Total\ Volume\ of\ fresh\ soil\ sample}\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

Porosity was determined indirectly from the measured bulk density and particle density values and using the equation below (Baver et al., 1972);

$$\text{Total porosity Total porosity} = 1 - \left(\frac{Bulk\ density}{Particle\ density}\right) \times 100\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Determination of Organic Matter Content

Walkley-Black wet combustion method was employed in Organic carbon determination in which the soil samples were treated with standard $K_2Cr_2O_7$ and Conc. H_2SO_4 and was titrated with standard ammonium sulphate solution ($(NH_4)_2SO_4$). After Organic Carbon, has been determined, the result was multiplied by a factor 1.72 to get the organic matter content of the soil (Jones, 2001).

Data Analyses

All data collected were subjected to Analysis of Variance (ANOVA) and analysed using Statistical Analyses System (SAS 9.4 SAS system for windows by SAS Institute Inc., Cary, NC, USA). Analysis of Variance (ANOVA) was used to determine the significant treatment effect on the measured properties with a significant difference of $p<0.05$. Duncan Multiple Range Test (DMRT) was used for mean separation.

Results and discussion

Soil Organic Matter (SOM) Content of the Soils

The interaction between sampling spots (SS) and sampling depth (SD) on the OM was significant ($p<0.001$) and is shown in Figure 2a. The interaction between the SS and SD differed significantly ($p<0.001$) from one SS to another with the highest (2.1%) in spot E at 0-15 cm while the lowest was obtained in spot D at 15-30 cm depth with 1.43%. Spot E had an increase of 32% of OM than spot D. Higher OM was recorded in spot E than other SS irrespective of the SD. The increase in OM over other SS ranged from 6.1-32%. The mean values of the sampling spots differed significantly from one sampling spot to another in the order of E>C>F>B>A>D with E having an increment of 5.1%, 17.5%, 18%, 18.5%, and 20.6% of OM over C, F, B, A, and D, respectively (Table 1). As indicated in Figure 1, spot C was also near a shelterbelt, which could be attributed to the relatively higher OM content of the spot. Spot E was found to differ significantly ($p<0.05$) from spot C with only 6.1% which was the least of the differences when compared with other SS. There was no significant difference ($p>0.05$) between spots A, B, D and F at 0-15 cm. Non-significant ($p>0.05$) difference between the spots (A, B, D and F) depicted the clear condition of the farm in terms of OM content, because there was no external influence, as is the case in spots C and E that are continually being influenced by forest leaf litters from the nearby trees. No significant difference ($p>0.05$) was observed from spots C and E at 15-30 cm depths, but they differed from their counterpart SS at the same depths. Averagely, significantly higher ($p<0.001$) OM was found in the upper depth (0-15 cm), which differs from the lower depth (15-30 cm), with 12.2% increased (Table 1). The study agrees with Liebig et al. (2005) and Nabayi et al.

(2019c), who found greater soil organic carbon at the upper depth of 0-5 cm depth when compared to the lower depth. It also agrees with Creswell and Hamilton (2002) who reported that OM weighs much less per unit volume than soil minerals; soil high in organic matter have lower particle density than soil similar in texture but low in organic matter. Hillel (1998) reported that organic matter is an important component of soil solid, which directly influences the physical and hydraulic properties of soil. Organic matter, which is usually in small quantity in soil, has a profound influence on the physical and chemical properties of mineral soils (Blanco-conqui et al., 2006). It promotes the formation and stability of soil structure and increases water retention, infiltration, and drainage (Koorevaar et al., 1983).

Table 1. *Analysis of variance (ANOVA) and main effect means for organic matter, bulk density, particle density and total porosity. Main effects are sampling spots and sampling depth*

	ANOVA P>F			
Source of Variation	***OM***	***Pd***	***Bd***	***TP***
Replication (R)	.204	.267	.353	.936
Sampling spot (SS)	.001	<.001	<.0001	.013
Sampling depth (SD)	.001	.100	<.0001	.001
SS*SD	.001	.011	.002	.146
Sampling spots	Means			
A	1.58c	2.638b	1.438a	45.5ab
B	1.59c	2.640b	1.438a	46.2ab
C	1.84b	2.626c	1.411c	46.0ab
D	1.54d	2.653a	1.435ab	46.3ab
E	1.94a	2.625c	1.40d	46.5a
F	1.60c	2.631bc	1.42b	45.2b
SE (±)	*0.04*	*0.003*	*0.009*	*0.33*
Sampling depth (cm)	Means			
0-15cm	1.80a	2.63a	1.40b	46.7a
15-30cm	1.58b	2.64a	1.44a	45.2b
SE (±)	*0.03*	*0.002*	*0.004*	*0.19*

Mean comparisons were made only when *P* values for the main effects were ≤0.05. Means followed by different letters within the same column differ significantly from one another at 5% level of significance.

Effect of SOM on Particle Size Distribution of the Soils

Table 2 shows that the soil of the dryland farm is predominantly sandy in texture across the SS at different SD. At the depth of 0-15cm, the SS had a range of sand, silt, and clay of 93-96%, 1-2%, and 2-5%, respectively, with a textural class of sand. At 15-30 cm depth, the soils had a range of 81-91% sand, 2-7% silt, and 6-13% clay, with a textural class of sandy loam. All the SS at 15-30 cm SD were found to be sand apart from spots C and E, which were sandy loam in texture. Differences in textural class observed in spots C and E was attributed to the higher OM content obtained in the SS (Figure 2a), and this was due to their proximity to the shelterbelt. The forest litters from the shelterbelt had influenced the texture of some part of the farm to the extent of altering the textural class of the soil, particularly spots C and E. The two SS (C and E) had the highest content of clay (C=12%, E= 13%), silt (C= 6%, E= 7%) but least in sand percentages when compared with the other SS (Table 2). The result agrees with Jones and Wild (1975), who reported that soils in savannah are predominantly sandy.

Table 2. *Means of Particle Size Distribution and Textural Class of the Spots at Different Depths*

Particle size distribution	***Sand (%)***		***Silt (%)***		***Clay (%)***		***Textural class***	
Sampling spots	0-15 cm	15-30 cm	0-15 cm	15-30 cm	0-15 cm	15-30 cm	0-15 cm	15-30 cm
A	96^{a}	89^{a}	2^{a}	5^{a}	2^{b}	6^{bc}	Sand	Sand
B	96^{a}	91^{a}	2^{a}	2^{b}	2^{b}	7^{b}	Sand	Sand
C	93^{a}	81^{b}	2^{a}	6^{a}	5^{a}	13^{a}	Sand	Sandy Loam
D	94^{a}	91^{a}	2^{a}	2^{b}	4^{a}	7^{b}	Sand	Sand
E	95^{a}	81^{b}	2^{a}	7^{a}	3^{ab}	12^{a}	Sand	Sandy Loam
F	95^{a}	90^{a}	2^{a}	2^{b}	3^{ab}	8^{b}	Sand	Sand
SE (±)	*1.33*	*0.67*	*0.30*	*0.3*	*0.44*	*0.33*		

Means followed by the same letters within the same column are not significantly different from each other at 5% level of significance according to DMRT.

Effect of SOM on True Particle Density (Dp) of the Soils

The result of the main and interaction effects of SS and SD on Pd is presented in Table 1. The SS and SD interaction on Pd was significant ($p<0.01$) and is shown in Figure 2b. The mean values of the particle size analysis, Pd, Bd, and TP at the two different SD is presented in Table 3. The highest Pd was recorded in spot D (2.66 Mg m^{-3}) at 0-15 cm which differed significantly ($p<0.01$) from other SS, while the lowest was recorded in spots C and E with 2.62 and 2.61 Mg m^{-3}, respectively at 0-15 cm SD. Higher Pd is an indication of low OM content of the soil been part of the soil solid (Schjønning et al., 2017). The results agree with OM results in Figure 2a, which indicated that spot D at 15-30 cm had the least OM content (1.43%) than its other SS counterparts. The low OM in spot D was translated into significantly higher Pd than the other SS irrespective of the SD. Spot D had an increase of 2% of Pd over spot C been the SS (D and C) with the highest and the lowest Pd. The mean values of the Pd differed significantly ($p<0.01$) from one another in the order of D>B>A>F>C>E with D having an increment of 0.7%, 1.0%, 1.1%, 1.2% and 1.3% of Pd over B, A, F, C, and E, respectively. SD wise, there was no significant difference ($p>0.05$) in terms of Pd with the higher Pd value in the 15-30 cm and lower in the 0-15 cm, as shown in Table 3. The result agrees with London (1991) and Brady and Weil (2002) who reported that soil particle density generally increases with soil depth because of the concurrent decreases in organic matter. Changes in soil particle density take a longer time to occur, and it depends on the management activities been carried out on a particular soil (Blanco-conqui et al., 2006).

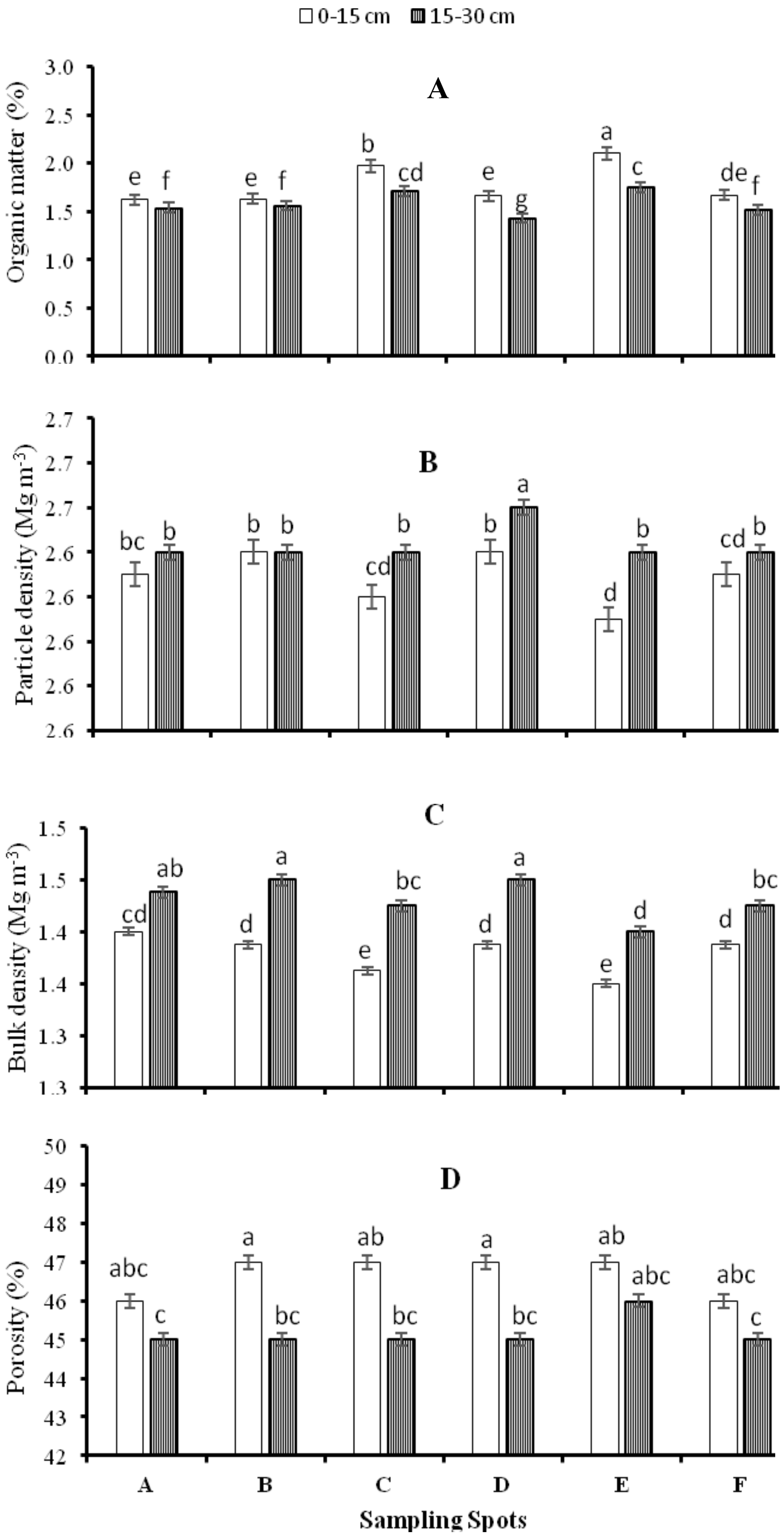

Figure 2. *Effect of Sampling spots and sampling depths on (A) organic matter, (B) particle density, (C) bulk density and (D) total porosity of a dryland soil. Bars indicate the standard error. Means with same letters are not significantly different according to DMRT at 5%.*

Therefore, the differences observed from one spot to another in the present study were attributed to the location differences. Spots C and E have benefitted to the presence of the shelterbelt which improved the OM of the soil area thereby making the density of the soils to be less, and this agrees with Schjønning et al. 2017 and Ruehlmann and Körschens (2020) who stated that type of soil mineral present and amount of OM affects the Pd of an area.

Table 3. *Means (±SE) of True Particle Density and other Physical Properties of the Soils*

Physical properties	***0-15 cm***	***15-30 cm***
Sand (%)	95 ± 0.70^{a}	87 ± 1.67^{b}
Silt (%)	2 ± 0.04^{b}	4 ± 0.50^{a}
Clay (%)	3 ± 0.33^{b}	9 ± 1.00^{a}
Textural class	Sand	Loamy sand
Particle Density (Mg m^{-3})	2.63 ± 0.08^{a}	2.64 ± 0.01^{a}
Bulk density (Mg m^{-3})	1.40 ± 0.007^{b}	1.45 ± 0.01^{a}
Porosity (%)	47 ± 0.33^{a}	45 ± 0.03^{b}
Organic matter (%)	1.78 ± 0.08^{a}	1.59 ± 0.06^{b}

Means with same letters across the same row are not significantly different from each other at 5% level of significance according to DMRT.

Effect of SOM on Bulk Density (Bd) of the Soils

The main effects of SS and SD is presented in Table 1. The results showed that there was a significant effect of SS and SD, as well as their interaction on the soil Bd ($p<0.01$). The result of the interaction (Figure 2c) showed that higher Bd values were obtained in spots A, B, and D at 0-15 cm with 1.45, 1.46, and 1.46 Mg m^{-3} each, respectively, while the lowest was found in spots C and E at 0-15cm. Spots C and E had a Bd of 1.39 and 1.38 Mg $m^{-3,}$ which differ significantly ($p<0.01$) from other SS irrespective of the SD. Spots A, B, and D had a Bd increment of 5.5% over spots C and E. Similar to Pd results, OM had influenced the Bd of the soil with spots C and E been richer in OM with a consequent reduction in their soil densities. Table 3 also shows that averagely, there was a significant difference ($p<0.01$) between the two SD. The higher Bd was recorded at the 15-30 cm with a 2.7% increment over its 0-15 cm counterpart. The higher Bd is equally attributed to the OM contents of the depths with higher OM in the upper depth (0-15 cm), which rendered the soil low in Bd. This result agrees with Han et al. (2006) and Nabayi et al. (2019b), who observed that increases in organic matter content leads to lower bulk density (Bd) of a soil. The result also is in line with research findings by Zaibon et al. (2016), who reported higher Bd with an increase in depth. Variation in Bd was attributed to the relative proportion and specific gravity of solid organic and inorganic particles and the porosity of the soil (Hossain et al., 2015). Similarly, Bd increases with an increase in depth due to consequent reduction in porosity (Creswell & Hamilton, 2002).

Effect of SOM on Total Porosity (TP) of the Soils

The main effects of SS and SD on TP is presented in Table 1. The result of interaction between the SS and SD on TP was significant ($p<0.001$) and is shown in Figure 2d. The result showed that the highest was recorded in spots B and D at 0-15 cm, each with 47%, which did not differ significantly ($p>0.05$) from spots C and E at the same depth. The lack of significant difference between the spots was due to the higher Pd and Bd of spots B and D and lower Pd and Bd of spots C and E, as shown in Figure 2b and 2c. The amount of pore space is determined largely by the arrangement of the solid particle (Nabayi et al., 2017). The interaction results indicated a lower TP in virtually all the SS at 15-30 cm with the exception of spot E at the same SD, which had a 2.1% increase over its SD counterpart. However, there was no significant difference ($p>0.05$) between all the SS at 15-30 cm SD despite recording (spot E) higher than its counterpart. The improvement in the TP in the sampling spots C and E despite lower Pd values (Figure 2b) than their counterparts was due to the concurrent decreased in the Bd of the sampling spots bacause to the higher OM content of the spots.

Table 4. *Correlation matrix table for the measured soil physical properties at 0-15 and 15-30 cm soil depths*

	0-15 cm					
	Bd	**Pd**	**TP**	**OM**	**SND**	**CLAY**
PD	0.833*					
PR	-0.600 ns	-0.110 ns				
OM	-0.978***	-0.916*	0.488 ns			
SND	0.492 ns	0.268 ns	-0.442 ns	-0.476 ns		
CLAY	-0.492 ns	-0.268 ns	0.442 ns	0.476 ns	-1.000***	
	15-30 cm					
	Bd	**Pd**	**TP**	**OM**	**SND**	**CLAY**
PD	0.485 ns					
PR	-0.807*	-0.200 ns				
OM	-0.798 ns	-0.625 ns	0.666 ns			
SND	0.805 ns	0.388 ns	-0.625 ns	-0.935**		
CLAY	-0.743 ns	-0.307 ns	0.530 ns	0.875*	-0.945**	

*Significant at 5%, **Significant at 1%, ***Significant at 0.1%

Bd-Bulk density, Pd-Particle density, TP-Porosity, OM-Organic matter, SND-Sand.

The higher the Bd, the lower the TP and vice versa, but this is only applicable when using a constant Pd for the estimation of soil TP. The results also stressed the importance of including Pd measurement into routine analyses of physical properties because using a constant value may lead to a wrong assumption. Averagely, the main effect of SD shows that the higher TP was obtained in 0-15 cm with 46.7%, which differs significantly ($p<0.01$) from 15-30 cm that had 45.2%. The higher TP in the upper depth (12.2% increased over lower depth) could be attributed to the higher OM of the SD, which differs significantly from the lower depth (Figure 2a). Higher OM content decreases soil density, which in turn increases soil pore spaces (Nabayi et al., 2017). Sanchez (1976) reported that changes in soil structure alter the proportion of the soil pore spaces.

The Pearson correlation also indicate that OM had a significant ($p<0.05$) positive correlation with clay% ($r=0.87$) content at a depth of 15-30 cm (Table 4) but it is negatively correlated with Pd ($r=-0.91$) and Bd ($r=-0.97$) at 0-15 cm depth (Table 4). The result of the correlation indicated that increases in OM content would increase clay content of the soil, thereby increasing the CEC of the soil in one hand and the increase in OM content would also leads to a decrease in Pd and Bd of the sandy soil on the other hand. The result agrees with Kuoe and Joñczyk (2008) and Mikha et al. (2006) who reported that increase in TP is among the physical benefits of SOM.

Conclusions

The present study revealed that Pd of a sandy soil particularly dryland farm that is in proximity with shelterbelt- is not a constant value, and therefore, it changes in space and with time depending on the cropping system and the type of soil management practices employed. However, the present study showed that Pd is within the range reported in the literature (2.60-2.70 Mg m^{-3}) for sandy soils. Similarly, the study disclosed that higher Pd of a soil is an indication of lower TP and higher Bd as well. On the one hand, OM greatly influenced Pd and other physical properties of the soils as the SS with higher OM shown to have lower Pd, Bd, and higher TP. The negative correlations between OM with Pd and Bd signifies the importance of OM in improving the soil physical condition of the dryland farm.

Recommendations

The present study, therefore, recommends the inclusion of Pd measurement into a routine soil analysis if soil is suspected or known to be under OM influence (increased) because using the constant value to estimate some soil properties that relate to it, would be under or overestimated. It also further suggests that the addition of organic matter into the soil system in form of crop residues, manure, planting of legumes, and adoption of reduced/zero tillage would help improve the soil properties of the farm.

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Soils over Calcareous Rocks in Golo Burdo Mountain

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Abstract

The paper deals with calcareous soils in Golo Bardo Mountain in western Bulgaria. Until now no significant studies have been made for the soils of Golo Bardo Mountain. Our goal was to give assess data for their soil features, characteristics, main diagnostic indicators and properties in order to define the soil formation processes, as well as their complete morphological description. Eight soil profiles were studied in different parts of the mountain. Due to the carbonate soil-forming rocks, the leaching processes in these soils are extremely weak and it is usually difficult to distinguish the individual genetic horizons. In relation to the soil-forming carbonate rocks in the area, we distinguish two main soil units. The studied soils are Leptosols or Phaeozems with good fine-granular structure, dark humus horizon (mollic) and shallow soil profile Ak-ACk-CRk, lying on hard or weathered carbonate rock. In the studied mountain area with different elevation, the surface mollic horizon is usually shallower and very often eroded with fragments from calcareous rock. The soils are well stocked with organic matter. The amount of organic carbon in the surface A horizon varied from 7.4 % to 2.8%.

The calcium dominates in exchange capacity of the soil over all other cations. There is no exchange acidity in these soils, except small amounts in the soil surface and in litter. The content of carbonates is an important soil-forming feature of these soils.

Keywords: Leptosols, Phaeozems, carbonates, soil properties

Introduction

Golo Bardo Mountain rises is located between the towns of Pernik and Radomir and their valleys. The mountain is a part of the "Verilo-Rui" mountain range, the formation of which began at the end of the Mesozoic period, intensified during the Tertiary, when the current mountain was formed and continues to present days. It is composed mainly of Triassic sandstone, marl, limestone, conglomerates and etc. (Geography of Bulgaria, 2002). Carbonate rich content of the soil-forming rocks is with particular importance for determining the soil-forming process. Soil formation and distribution are mainly related to the chemical and mineral composition of the carbonate parent rock as well as to its physical, chemical and mineral properties (Donov, 1993; Ilinkin et al. 2017; Malinova et al., 2018; Teoharov, 2019). The main soil unit of this area is Rendzina, which could be classified as Rendzic Leptosols and Rendzic Phaeozems (IUSS Working group 2015).

According to Belivanova (1997), the main diagenetic processes that have affected the Triassic carbonate rocks are discussed in this study: transformation of metastable carbonates (aragonite and high-magnesium calcite) into calcite; compaction; cementation; recrystallization; authigenic mineral formation (dolomitization, silicification, albitization and pyritization). The Triassic sediments in Golo Bardo are incorporated in several groups: the Petrohan Terrigenous group, the Iskar Carbonate Group, and a very limited Moesian Terrigenous- Carbonate Group, which is out of the area of the section (Ilieva, 2017).

The soils from the area of Golo Bardo Mountain are formed under forest meadows, bushes and trees vegetation. As a typical mountainous terrain, surface horizons are subjected to erosion processes. The properties and composition of the studied soils and the degree of their fertility depend a lot on the type and age of the parent rocks, on the relief, exposure, latitude and altitude.

As well as on the impact of climatic conditions that activate or suppress more or less biological activity and determine the state and biological potential of soil cover (Koinov, 1947).

In the semi-mountainous areas, shallow forest soils have been developed on weathered hard rocks such as Rendzic and Clacaric Leptosols, and in many places they are also found in a complex with Endoclacic Phaeozems. Leptosols have a shallow profile (up to 30 cm) and often rocks on the surface. These soils occupy mostly rugged (erosion-hazardous) steep terrains and they are particularly not important for agriculture. The vegetation which is developing on them is mainly mixed forests. There are also coniferous trees, as well as shrubby, meadow-grass and in some areas - mosses and lichens. The soils are usually distributed in the foothills and mountainous areas of Golo Bardo and they are subjected to gully erosion.

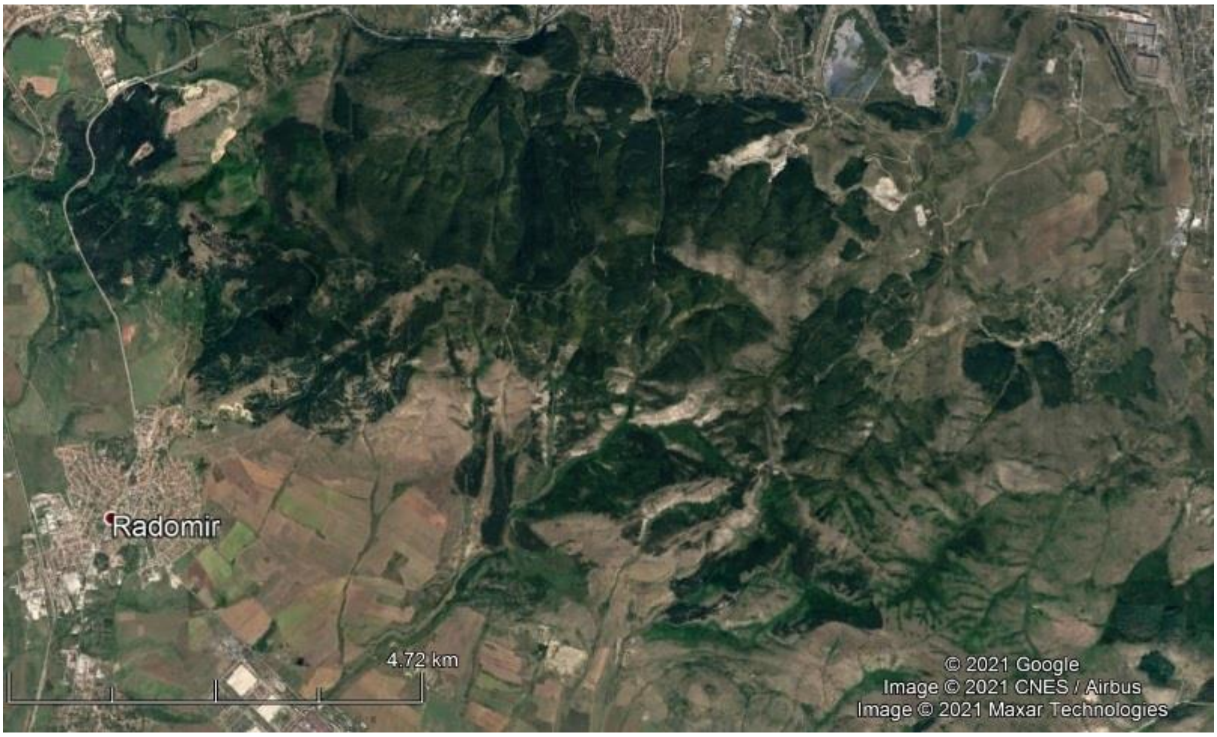

Figure 1. *Golo Burdo Mountain – district of Pernik, Bulgaria*

The anthropogenic impact play a key role for the genesis, structure and fertility of these soils. This includes deforestation, construction in forest areas, stone quarries, excavation of mountain areas for coal and other minerals, road construction and permanent pollution. From Golo Bardo mountain are produced raw materials such as limestone and dolomite, used for cement production. Sand quarries have been discovered in several places near rivers.

The aim of the study is to establish the contemporary development of the soils on Triassic carbonate sediments and to describe their main morphological, chemical and physical properties.

Material and Methods

To establish the criteria and diagnostics for the classification of Rendzinas – Rendzic Leptosols and Rendzic Phaeozems (IUSS Working group, 2015), in this article we used previous data from studies in the area of Golo Bardo mountain. In addition to in-depth geomorphological and morphological studies, analytical results are given on various diagnostic indicators.

Eight soil profiles were studied in the different parts of the mountain. The analysis of soil samples was performed according to the following indicators, criteria and methods: Morphological description of soil horizons and characteristics (Teoharov et al. 2019, Guidelines for soil description, Jahn, et al., 2006). Soil texture by Kachniski (1958), transformed to USDA classes; Total carbon according to Tyurin (Kononova, 1966); Total nitrogen according to Keldal (Penkov et al., 1991); total carbonates by the Scheibler (Penkov et al., 1991); Cation exchange capacity, exchange cations and degree of base saturation (Ganev and Arsova, 1980). Ammonia and nitrate nitrogen by Bremner and Keeney (1966); the mobile forms of phosphorus and potassium by the acetate-lactate method of Ivanov (1984) and pH and EC, in water with combined "pH and EC device", Microsoft Excel (2010) is used for figures and statistics.

Results and Discussion

Clacareous soils spread in the mountain such as Rendzic or Calcaric Leptosols and Endocalcic Phaeozems, are soils are rich in carbonates (up to 52 %, Table 2) but also with high organic carbon content due to alkaline reaction, in which the decomposition of organic matter is slow and the soil accumulates high amounts of stable organic matter (Table 1). Their rich carbonate content is due to Triassic calcareous sediments over which they were developed (limestone, dolomite, marl, etc.). In previous edition of FAO (1988) classification these soils were known as Rendzinas.

Due to the carbonate soil-forming rocks, the leaching processes in these soils are extremely weak and it is usually difficult to distinguish the individual genetic horizons. In relation to the soil-forming carbonate rocks in the area, we distinguish two main units of these soils in Figure 1. The geologic or lithological nature of the parent material was considered to be the most important soil forming factor in determining the type of soil formation (Handley, 1954).

The profiles 1 and 8 are classified as Rendzic Leptosol which are characterized by a good fine-granular structure dark humus horizon (mollic) up to 15-20 cm and shallow soil profile Ak-ACk-CRk with a thickness of 20-40 (up to 75) cm, directly lying on hard or weathered carbonate rock. In the studied area of the mountain with different elevations, the surface mollic horizon is usually shallower and very often eroded with fragments from parent rock. The other Leptosols are Skeletic Calcaric Leptosol in most of them with shallow mollic horizons (IUSS Working group, 2015).

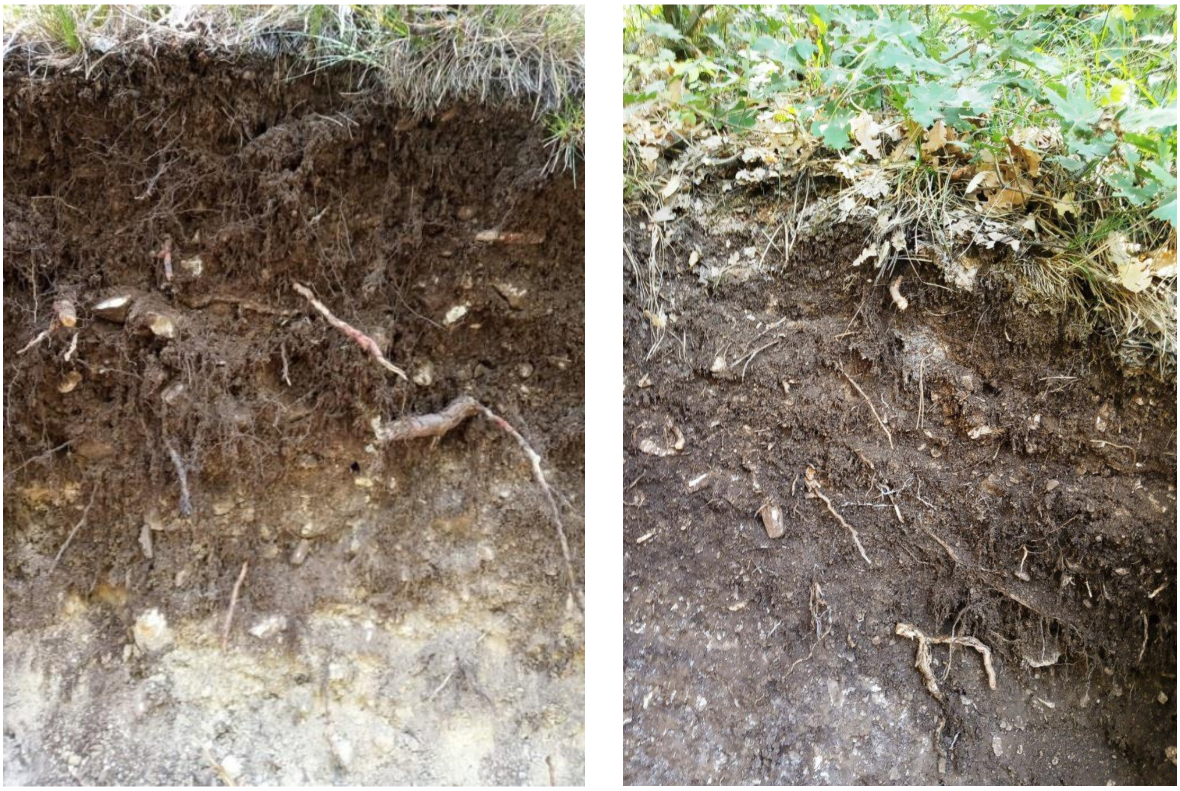

Figure 2. *Calcareous soils from Golo Bardo Mountain. Profile 8 - Rendzic Leptosol (on the left) and Profile 3 – Endocalcic Phaeozem loamic (on the right).*

Leptosols are highly incoherent while Phaeozems are highly coherent, leading to the conclusion that the physical and chemical properties of the soil profiles of Phaoeozems are specific (Radmanovic et al., 2020).

Phaeozems are deep soils form 70 to 120 cm soil profile with A1(Ak1)–Ak2-ACk-Ck-R structure and usually thick surface mollic horizon. These soils have primary carbonates from weathering rock. Most of the soil profiles they are leached in depth, but not anywhere. Mollic horizon is well formed, dark colored with fine granular structure and deeper about up to 30-50 cm. In whole profile stony fragments from parent rock could be found also. Phaeozems are spread usually in the low accumulative part of the mountains, so called foothills and land pockets. In such areas soil erosion is weak and consequently deep soil profiles could develop.

The soils are well stocked with organic matter, under the influence of forests vegetation. The amount of organic carbon in the surface A horizon is between 7.4 % and 2.8%. The mean value of org. C is 3.28 % in all soil horizons (Table 3). These soils are developed under dry conditions where organic carbon accumulation is greater than decomposition as a result of the limestone-rich environment, and where a portion of the organic component might be derived from residues of bedrock weathering (Schreier et al., 1985). The temperate climatic conditions create a favorable condition for intensive humification with the formation of good quality humus (Hristov et al., 2017; 2021) .

Table 1. *Main soil chemical and physical properties.*

	Horizon Depth (cm)	**Total org. C %**	**Total N %**	**C/N**	**Carbo-nates, %**	**NH_4+NO_3 mg/kg**	**P_2O_5 mg/100g**	**K_2O mg/100g**	**Soil texture in mm**		
									Sand >0.05	Silt 0.05-0.002	Clay <0.002
Profile 1. Rendzic Leptosol loamic											
1	Ak 0-5	7.14	0.41	17.54	25.3	37.4	3.4	36.8	40.5	38.5	21
2	ACk1 25-20	2.53	0.25	9.92	38.4	23.0	1.2	22.1	39.1	40.95	19.95
3	ACk2 20-38	1.26	0.15	8.23	40.3	20.2	1.4	8.3	44.7	38.45	16.85
4	Ck 38-70	0.5	0.06	8.33	51.7	19	4.8	6.5	35.1	43.55	21.35
Profile 2. Skeletic Calcaric Leptosol loamic											
5	ARk 0-19	5.35	0.46	11.5	5.06	23.0	0.23	51.9	36.5	39.7	23.8
Profile 3. Endocalcic Phaeozem loamic											
6	Ak1 0-10	6	0.6	10.03	6.96	9.79	0.32	71	53.2	28.65	18.15
7	Ak2 10-22	3.4	0.41	8.35	14.7	21.3	0.23	47..6	54.1	29.65	16.25
8	Ak3 22-43	2.89	0.35	8.16	16.49	23.0	0.21	20.6	52.7	28.9	18.4
9	ACk 43-60	1.97	0.23	8.38	19.44	21.3	0.21	9.8	50.5	30.15	19.35
10	Ck 60-100	1.14	0.12	9.57	29.4	20.2	0.22	6	48.7	29.85	21.45
Profile 4. Mollic Calcaric Leptosol loamic											
11	A 0-10	7.8	0.49	16.01	1.18	17.3	0.24	23.6	52.9	30	17.1
12	ACk 10-28	4.08	0.38	10.59	1.29	19.0	0.23	15.7	47.7	35.2	17.1
13	CRk 28-70	2.86	0.35	8.19	3.85	17.8	0.21	34.6	49.3	32.1	18.6
Profile 5. Skeletic Calcaric Leptosol loamic											
14	ARk0-14	3.47	0.35	10.26	10.26	19.0	0.3	10.2	52.3	29.25	18.45
Profile 6. Cambic Mollic Calcaric Leptosol clayic											
15	Ak 0 - 5	2.68	0.27	9.93	2.25	22.5	1.3	26.8	14.7	35.1	50.2
16	ACk1 5 -30	1.85	0.20	9.25	23.41	10.9	0.21	14.9	35.8	19.55	44.65
17	ACk2 30-50	2.09	0.21	9.95	21.55	20.2	0.23	13.5	31.7	22.9	45.4
18	Ck 50 - 75	1.13	0.14	8.07	24.04	15.6	0.3	8.7	29.5	20.95	49.25
Profile 7. Endoclacic Phaeozem clayic											
19	Ak 0 - 9	6.63	0.52	12.75	2.25	13.2	0.3	55.1	51.1	18.75	30.15
20	Ak2 9 -32	4.2	0.39	10.77	4.9	8.60	0.8	32.8	46.9	14.85	38.25
21	ACk1 32–45	3.29	0.34	9.68	12.26	14.4	1.6	22.4	53.4	14.9	31.7
22	ACk2 45-61	2.86	0.29	9.86	10.51	23.6	1.4	20.8	48.1	13.05	38.85
23	Ck1 61 - 90	2.36	0.23	10.26	18.77	15.5	1.2	18.5	34.2	17.55	48.25
24	Ck2 90-120	2.09	0.22	9.50	22.58	11.5	0.9	23	39.2	18.15	42.65
Profile 8. Rendzic Leptosol											
25	Ak 0 -11	5.33	0.51	10.45	18.77	12.1	0.1	33.5	42.9	17.05	40.05
26	ACk 11 -30	3.52	0.37	9.51	20.63	9.2	0.3	30	50.6	12	37.4
27	Ck 30 - 75	0.4	0.05	8.00	43.1	11.5	1.6	5	51.6	12.05	36.35

Table 2. *Cation exchange capacity of exchange cations, base saturation and electrical conductivity.*

	Horizon / Depth cm	**pH / H2O**	**EC mS/cm**	**CEC**	**Ex. H$_{8.2}$**	**Ex. Al**	**Ex. Ca**	**Ex. Mg**	**Base Saturation %**
				mequ / 100g soil					
Profile 1. Rendzic Mollic Leptosol loamic									
1	Ak 0-5	6.7	0.105	40.6	2.2	0.0	36.8	2.5	94.58
2	ACk 5-20	7.25	0.098	30.0	1.0	0.0	26.5	3.0	96.67
3	ACk$_2$ 20-38	7.5	0.077	26.0	0.0	0.0	22.2	3.8	100.00
4	Ck 38-70	7.65	0.07	25.0	0.0	0.0	21.2	3.8	100.00
Profile 2. Skeletic Calcaric Leptosol loamic									
5	ARk 0-19	7.0	0.098	48.4	1.6	0.0	43.5	3.8	96.69
Profile 3. Endocalcic Phaeozem loamic									
6	Ak$_1$ 0-10	7.0	0.105	45.8	2.0	0.0	39.5	4.8	95.63
7	Ak$_2$10-22	7.25	0.126	38.8	1.0	0.0	33.8	4.2	97.42
8	Ak$_3$22-43	7.40	0.119	36.7	0.0	0.0	32.2	4.5	100.00
9	ACk43-60	7.40	0.112	30.6	0.0	0.0	26.1	4.5	100.00
10	Ck 60-100	7.50	0.084	30.6	0.0	0.0	25.6	5.0	100.00
Profile 4. Mollic Calcaric Leptosol loamic									
11	A 0-10	6.6	0.07	44.2	4.1	0.0	35.6	4.6	90.72
12	ACk 10-28	7.1	0.084	47.1	2.0	0.0	40.8	4.8	95.75
13	CRk 28-70	7.4	0.091	36.0	0.0	0.0	31.0	5.0	100.00
Profile 5. Skeletic Calcaric Leptosol loamic									
14	ARk 0-14	7.4	0.091	49.6	0.0	0.0	44.8	4.8	100.00
Profile 6. Cambic Mollic Calcaric Leptosol clayic									
15	Ak$_1$ 0 - 5	7.4	0.098	26.0	0.0	0.0	24.8	1.2	100.0
16	ACk 5 -30	7.4	0.091	25.9	0.0	0.0	24.6	1.3	100.0
17	ACk 30 -50	7.4	0.098	26.3	0.0	0.0	25.0	1.3	100.0
18	Ck 50 - 75	7.5	0.084	26.7	0.0	0.0	25.4	1.3	100.0
Profile 7. Endoclacic Phaeozem clayic									
19	Ak$_1$ 0 - 9	7.2	0.168	48.6	1.0	0.0	42.0	5.6	97.94
20	Ak$_2$ 9 -32	7.4	0.126	48.6	0.0	0.0	42.5	6.1	100.0
21	ACk 32-45	7.4	0.105	39.0	0.0	0.0	33.0	6.0	100.0
22	ACk$_2$ 45- 61	7.4	0.091	37.8	0.0	0.0	32.0	5.8	100.0
23	Ck 61 - 90	7.4	0.105	36.8	0.0	0.0	30.6	6.2	100.0
24	Ck$_2$ 90 - 120	7.4	0.126	33.8	0.0	0.0	27.8	6.0	100.0
Profile 8. Rendzic Leptosol									
25	Ak 0 -11	7.4	0.119	41.8	0.0	0.0	37.0	4.8	100.0
26	ACk 11 -30	7.4	0.105	32.6	0.0	0.0	28.0	4.6	100.0
27	Ck 30 - 75	8.0	0.077	18.6	0.0	0.0	14.6	4.0	100.0

Soils developed over hard carbonate rocks, in contrast to other soils, have more specific distribution of carbonates. For example, the amount of carbonates in the whole profile varies from 1.2 to 52.2 % (Table 1 and 3). This suggests that the carbonate plate has a primary terrigenous origin. The reaction of these soils is alkaline (pH in water has the highest levels in the carbonate plate). Studied soils have form neutral reaction (6.7) up to slightly alkaline reaction (8.0). The reason for that is high content of carbonates. The pH is usually above 7, but in surface horizon sometimes it is lower because of high content of organic litter especially under pine forest trees (Table 2).

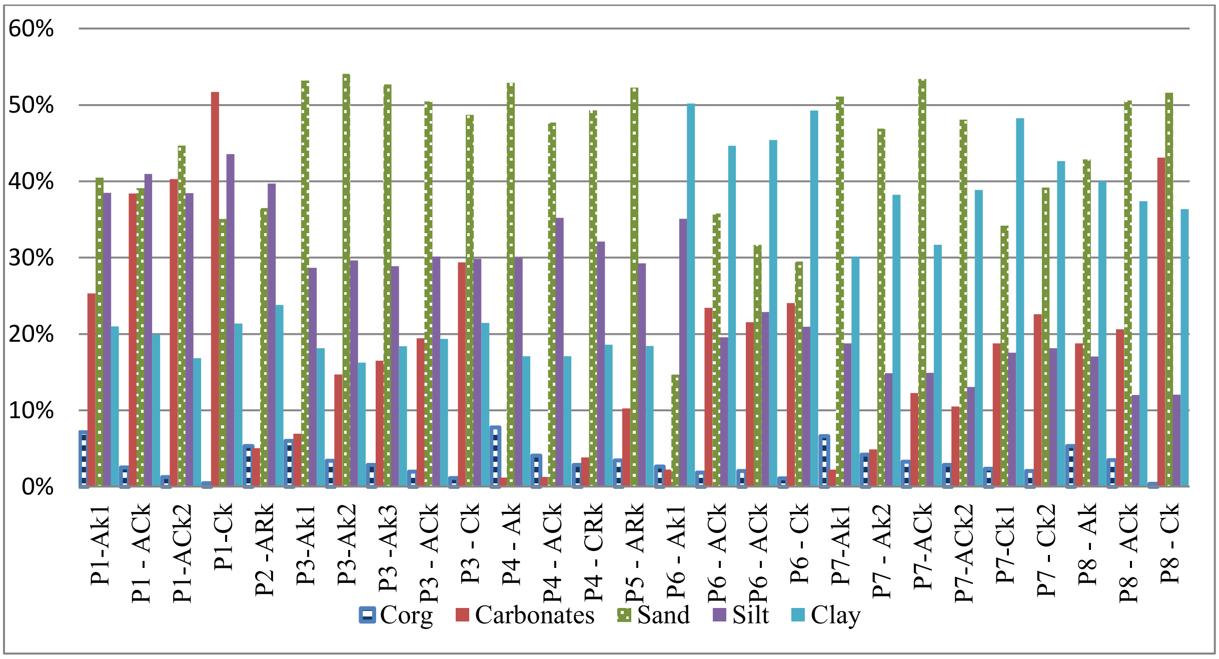

Figure 3. *Soil organic carbon, total carbonates, and particle sizes content.*

The soil mean pH = 7.33, could define as carbonate, very slightly alkaline. Compared to the colloidal reactivity (the mean value of CEC = 36.6 mequ/100g) is medium colloidal clay, with evolution to montmorillonite clay (Ganev et al., 1990). This determines the presence of alkaline carbonates and the active hydrolysis-alkaline adsorption salt composed of strongly based alkaline cations (Ca and Mg) and weakly acidic ion exchangers (mainly H^+).

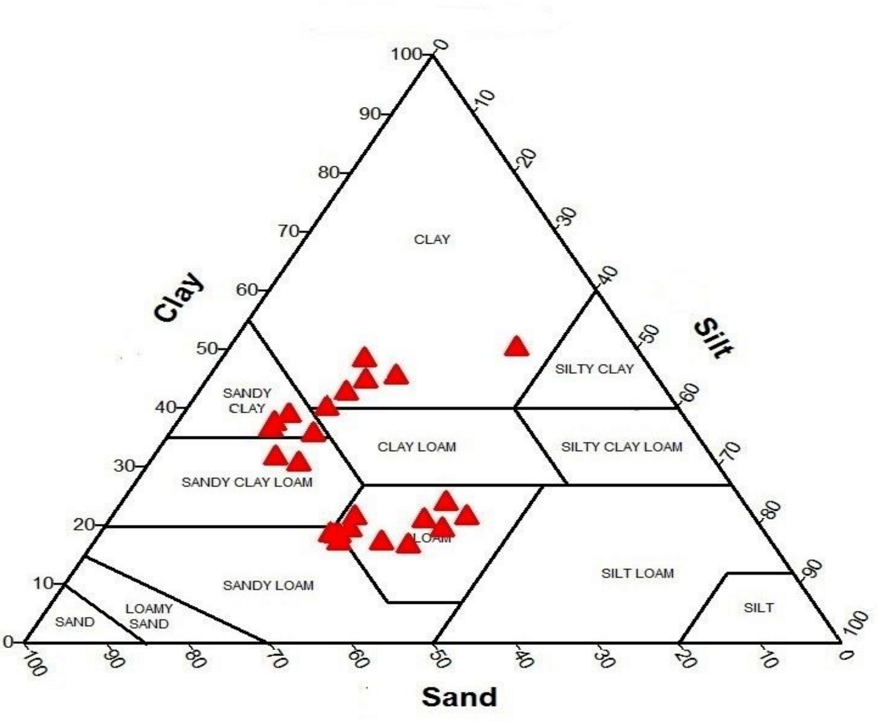

Figure 4. *Soil texture in all soil horizons and profiles.*

The total nitrogen varies from 0.60 to 0.35 %, in surface horizons which good reserve. Well known fact is that approximately 98% -99% of nitrogen is found in the soil in the form of organic nitrogen compounds (mainly in humus) and only 1% -2% - as available for plants nitrates and ammonium salts.

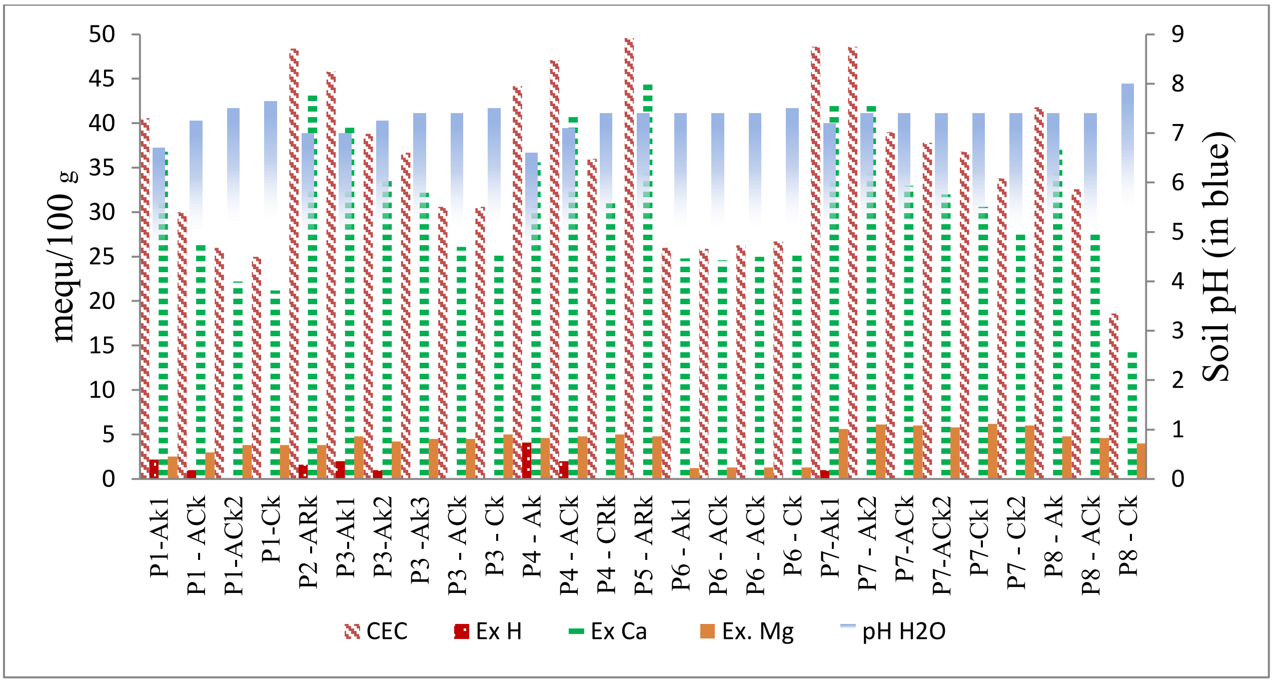

Figure 5. *Main physicochemical properties and soil pH(in blue)* .

Mobile forms of NH_4 and NO_3 are about from 37 to 8.6 mg/kg which is low. The reason for that is high content of carbonates and mobile forms of NH_4, NO_3 and P_2O_5 are blocked. Only available K_2O has high content (mean value about 25 kg/100g), which is typical for weathered mountain soils in Bulgaria.

The type of humus according to C:N ratio is Mull (<14). This type is characterized by of forests, or grasslands with humid climates. The porous, crumbly humus rapidly decomposes and becomes well mixed into the mineral soil, so that distinct layers are not apparent. Where free $CaCO_3$ occurred in the Ak-horizon, a mull forest horizon had developed even on coarse sand and the associated herb flora differed only slightly from that occurring on very acid mull. Mulls generally form under trees with more nutrient-rich litter, where gut-passage through soil animals followed by predominantly bacterial decomposition creates granular structures (Delecour, 1980).The soil texture is mainly loamy, sandy-clay and clay (Figure 4). The silt fraction is lower than other two fractions (Table 3). The highest mean value of the soil texture is sand with about 44 % with additional skeletal content. Sandy soils with a higher skeletal content are the soils developed on marble (Filcheva et al., 2014). Usually these soils are loose, warm and well-aerated. A significant part of them have an unfavorable water regime due to their shallow profile. In most areas there are rocks on the surface. The studied soils developed over Triassic carbonate plate are characterized by good physical properties.

The content of carbonates varies in a fairly wide range (1.8-50%). In order to be classified as Rendzinas (Rendzic), soil-forming materials must contain more than 40%

carbonates. Profile 1 and 8 have Rendzic properties according WRB (IUSS working group, 2015). The mean pH_{H2O} value ~7.45 determines the presence of alkaline carbonates and the active hydrolysis-alkaline adsorption salt, composed of strongly basic alkaline earth cations and a weakly acidic ion exchanger. There is no exchange acidity in these soils, except small amounts in the soil surface and in litter (figure 5).

Table 3. *Main descriptive statistic values of studied soil profiles.*

	pH H_2O	EC	CEC	ex. H	ex Al	ex Ca	ex. Mg	B.S. %	Org C
Mean	7.33	0.10	36.00	0.55	0	31.4	4.20	98.7	3.29
Stand. Err.	0.05	0.00	1.70	0.20	0	1.49	0.29	0.45	0.38
Median	7.40	0.10	36.70	0.00	0	31.0	4.60	100	2.86
Mode	7.40	0.11	26.00	0.00	0	*	4.80	100	2.86
Stand. Dev.	0.27	0.02	8.85	1.02	0	7.73	1.53	2.33	1.98
Range	1.40	0.10	31.00	4.10	0	30.2	5.00	9.28	7.40
Minimum	6.60	0.07	18.60	0.00	0	14.6	1.20	90.7	0.40
Maximum	8.00	0.17	49.60	4.10	0	44.8	6.20	100	7.80
	Total N	C/N	Carbonates	NH_4 $+NO_3$	P_2O_5	K_2O	Sand	Silt	Clay
Mean	0.33	10.37	18.12	17.78	0.87	24.80	43.96	26.36	29.66
Stand. Err.	0.04	0.85	2.63	1.19	0.21	3.20	1.83	1.87	2.32
Median	0.35	9.57	18.77	19.00	0.30	22.10	47.70	28.90	23.80
Mode	0.41	0.00	2.25	23.00	0.23	*	*	*	17.10
Stand. Dev.	0.16	3.05	13.66	6.18	1.08	16.60	9.53	9.74	12.06
Range	0.54	9.38	50.52	28.80	4.70	66.00	39.40	31.55	33.95
Minimum	0.06	8.16	1.18	8.60	0.10	5.00	14.70	12.00	16.25
Maximum	0.60	17.54	51.70	37.40	4.80	71.00	54.10	43.55	50.20

Because of high carbonate content studied soils have high Base saturation (98.6 %). The calcium dominates in base saturation over all other cations. The content of carbonates is an important soil-forming feature of these soils, because it diagnoses the base excess, and which the process of soil formation and carbon sequestration take place (Ganev, 1989).

Conclusion

The soils of Golo Bardo mountain are Rendzic or Calcaric Leptosols and Endocalcic Phaeozems, with high organic carbon content with alkaline reaction. Decomposition of organic matter is slow and the soil accumulates high amounts of stable organic matter. Their rich carbonate content is due to Triassic calcareous sediments over which they were developed. The Leptosols are characterized by a good granular structure dark humus horizon (mollic) up to 15-20 cm and shallow soil profile type Ak-ACk-CRk with a thickness of 20-40 (up to 75) cm, lying on hard or weathered carbonate rock. Phaeozems are deep soils form 70 to 120 cm soil profile with A1(Ak1)–Ak2-ACk-Ck-R structure with usually thick surface mollic horizon that is well formed, dark colored with fine granular structure and deeper. The type of humus according C:N ratio is Mull(<14). This type of humus is typical for forests, or grasslands in humid climates.

These soils have primary carbonates from weathering rock consequently they have high sorption capacity. The soil reaction varies from neutral and to slightly alkaline, with the high degree of base saturation. The calcium dominates in exchange capacity of the soil over all other cations. Soils have favorable properties due to good reserve of organic carbon, potassium, nitrogen and high base saturation

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Pedological Properties and Classification of Soils Underlain by Asu River Group Parent Materials in Ohaozara, Southeastern Nigeria

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Abstract

The study was carried out in Ohaozara Southern Ebonyi State in Southeastern Nigeria and aimed at studying the pedological properties as well as classifying the soils underlain by Asu River group parent material. Study area was identified in a rice soil of about 120 hectares used by FGN/IFAD Value Chain Development program (VCDP). Three profile pits were dug on a transect line of about 100 – 200m apart. Samples were collected and analyzed using standard procedures. Soil colours ranged from yellow (5YR7/3) at the A horizon to reddish yellow (5YR7/8) at the Bt2 horizon of pedon in location 1 when measured under dry condition. Also at the location 1 when soils were measured under moist condition, the colours ranged from very pale brown (10YR7/3) at the topmost horizon to reddish yellow (7.5YR7/8) at the Bt2 horizon. At location 2, soil colour ranged from white (5YR8/1) at the topmost horizon to reddish yellow (10YR7/6) at the Bt2 horizon when dry. However, when moist it ranged from light grey (7.5YR7/1) to strong brown (7.5YR5/6) from top to bottom of the profile. Location 3 had colours ranging from light grey (5YR7/1) at the top to yellow (10YR8/4) at the bottom when dry and from very pale brown (10YR7/3) to yellow (5YR7/6) from horizon A to horizon Bt2 when moist. Silt-clay ratios decreased down the profile in all investigated locations and scored means of 0.95, 1.02 and 1.10 in locations 1, 2 and 3 respectively. Bulk density and porosity had an opposite trend as bulk density increased down the profile, porosity decreased down the profile. The means of bulk density were 1.34, 1.44 and 1.32 g/cm^3 while the means of the porosity were 49.34, 45.66 and 50.17 % in locations 1, 2 and 3 respectively. Therefore, pedon 1 is classified as Typic Eutrudept (USDA) and Eutric Cambisols (WRB) while pedons 2 and 3 were classified as Aquic Eutrudepts (USDA) and Gleyic Leptosols (WRB).

Keywords: Pedological properties, soil classification, Asu river group, southeastern Nigeria

Introduction

Soil pedology focuses on understanding and characterizing soil formation, evolution, and the theoretical frameworks through which we understand a soil body(s), often in the context of the natural environment. Among the key components of pedological properties of the soil are the morphological, physical and chemical characteristics of the soil. Morphological, physical and chemical properties of the soils are of great importance in understanding how the soils could be properly utilized. Soil morphology is studied from the *in situ* evaluation of the soil profile while the physical and chemical properties are measured by laboratory techniques. For agricultural purpose, physical properties of the soils are not easily modified in the plantation (Ugwa et al., 2017). It is even harder to alter them than the chemical properties (Brady, 2002; Malgwi, et al., 2000). Different workers (Orimoloye, et al., 2010; Kamalu, et al, 2014), have associated yield decline to poor physical properties and these may include low soil depth, changes in water holding capacity and relatively light texture soils. Enwezor, et al., (1981) had reported that most soils of southern Nigeria are inherently low in soil fertility, very susceptible to erosion and acidic with poor physical properties.

A long continuation of wetland soil cultivation often causes characteristic changes in soil morphology and properties, including surface gray coloring and the development of iron and manganese accumulation horizons. The major morphological features such as grey or low chroma (<3) colour, mottles are characteristics of this soils, and is an indication of soil wetness brought about by oxidation – reduction cycle due to ground water fluctuation inter-relationship between these features. The reduced Fe present in these soils impact grayish colour on the soil matrix (Malgwi et al., 2000).

Soil characterization and classification provide a powerful resource for the benefit of mankind, especially in the area of food security and environmental sustainability (Esu, 2004). According to Ajiboye and Ogunwale (2010), studies conducted on the soils of some regions of Nigeria and subsequent classifications were based majorly on the soil parent materials at the higher category classes. Soil classification study is however a major building block in terms of understanding the soil, classifying it as well as getting the best understanding of the environment. Esu and Akpan-Idiok (2010), characterized the morphological and physico-chemical properties of alluvial soils and classified them according to the USDA Soil Taxonomy System (Soil Survey Staff, 1999) and the World Reference Base for Soil Resources (WRB) Classification System (FAO, 2001). Therefore USDA Soil Taxonomy (Soil Survey Staff, 1999) and the WRB for soil resources (FAO, 2001) are the two most used classification systems in Nigeria (Esu, 1999).

This study aimed at determining the morphological and physical properties of the soils derived from Asu River parent material as well as classify them for better management and agricultural sustainability.

The Study Area

Location

The study area is located near Umunaga – Uburu in Ohaozara Local Government Area of Ebonyi State Southeastern Nigeria, with the Latitude of 6^{o} 01′ N and Longitude of 7^{o} 78′ E. The study area is located within the partially modified low rain forest and wooded/ grassland derived savannah southeastern Nigeria and experiences rainfall between March - November with highest intensities occurring between June-September while about three months of dry season occur from December – February (Ogbodo, 2013). The area lies within the humid tropics with Ustic moisture regime (Obasi and Obasi 2020). This concept is one of moisture that is limited but is present at a time when conditions are suitable for plant growth. The soil in moisture control section in ustic moisture regime is dry in some or all parts for 90 or more cumulative days in normal year (Soil Survey Staff, 2003; Ahukaemere et al., 2018; Ahukaemere and Obasi, 2018). This location receives a mean annual rainfall of between 2250 mm in the South and 1500 mm in the northern part of the zone, average annual temperature of about 27^{o}C with relative humidity of 85% (Nwakpu, 2003).

Geology and Geomorphology

The study area falls within the Asu-River Geologic Group (Lower Cretaceous), Eze-Aku shale formation and Nkporo Formations. The Asu River Group is a major stratigraphic unit in the study area, consisting of dark micaceous shale, fine grained and calcareous sandstone bodies (Ogbodo 2013). The sediments later became folded given rise to two major structural features, the Abakalili anticlinorium and related Afikpo synclinorium (Esu, 2004; Ukaegbu and Akpabio 2009). It is made up mainly of hydromorphic soils which consist of reddish brown gravely and pale coloured clayey soil, shallow in depth, and of shale parent material (Obasi, 2010; Ogbodo, 2013).

Field Work

Reconnaissance study was carried out and the study area identified near Umunaga in Ogbuoma autonomous Community Uburu in Ohaozara Local Government Area of Ebonyi State. The study area was in a FGN/IFAD/ Value Chain Development Programme (VCDP) site having about 120 hectares of land. The study area has been subjected to rice farming over the years due its prevalent lowland nature. Three profile pits were dug at an appreciable interval of 100 – 200 m apart within the study area.

Laboratory Analysis

Soil samples were air dried, pulverized, and sieved through a 2 mm sieve mesh. The properties analyzed include particle size distribution determined by hydrometer method (Gee and Bauder, 1986). Soil pH was determined in a 1:1 soil/water ratio using digital pH meter and conductivity meter respectively. Exchangeable acidity was determined by the 1N KCl method. Exchangeable bases; Calcium (Ca), Magnesium (Mg), Potassium (K), and Sodium (Na) were determined using NH4OAc saturation method (IITA, 1979). Ca and Mg in solution were determined using Atomic Absorption Spectrophotometer, while K and Na were determined using Flame Emission Photometer. Organic carbon was determined by Walkley and Black dichromate wet oxidation method (Nelson and Sommers,1982). Total nitrogen was determined by micro-kjeldahl technique (Bremner and Mulvaney, 1982). The Effective Cation Exchange Capacity (ECEC) was determined summation method, while the available phosphorus was extracted by Bray II method (Olsen and Sommers 1982). Base saturation was calculated as the sum of all base forming cations, divided by cation exchange capacity and multiplied by 100.

Results and Discussion

The morphological properties of soils were as shown in table 1. The parent material is Shale/Alluvium derived from Asu River group (Ukaegbu and Akpabio 2009). The profiles were deep enough for rice cultivation and drainage indicated well drained for Ap and AB horizons and poorly drained for Bt1and Bt2 horizons. Soil colours ranged from yellow (5YR7/3) at the A horizon to reddish yellow (5YR7/8) at the Bt2 horizon of pedon in location 1 when measured under dry condition. Also at the location 1 when soils were measured under moist condition, the colours ranged from very pale brown (10YR7/3) at the topmost horizon to reddish yellow (7.5YR7/8) at the Bt2 horizon. At location 2, soil colour ranged from white (5YR8/1) at the topmost horizon to reddish yellow (10YR7/6) at the Bt2 horizon when dry. However, when moist it ranged from light grey (7.5YR7/1) to strong brown (7.5YR5/6) from top to bottom of the profile. Location 3 had colours ranging from light grey (5YR7/1) at the top to yellow (10YR8/4) at the bottom when dry and from very pale brown (10YR7/3) to yellow (5YR7/6) from horizon A to horizon Bt2 when moist. The coating of iron oxides often gives rise to yellow, brown or red colouration in the soil matrix and these may provide information on some soil properties. The low chroma observed in most of the epipedons may have resulted due to wetness situation of the studied soils, as FAO, (2006) noted that morphological feature such as low chroma is an indicative of soil wetness.

Table 1: Morphological Properties of Soils

Location	Colour	Colour	Structure	Consistence			Mottles	Root Abundance	Horizon Boundaries
1	(dry)	(moist)		Wet	Moist	Dry			
A	5 YR 7/3, y	10 YR 7/3, vpb	2,bk,c	s	fi	vh	-	C,m	clear
AB	5 YR 7/4, y	5 YR 6/1, pg	2,m,vc	vs	Vfi	eh	f	Mf,f	clear
Bt1	5 YR 7/8,r y	5 YR 7/6, ry	2,abk,c	vs	vfir	eh	m	Vf,f	Gradual
Bt2	5 YR 7/8,r y	7.5 YR 7/8, ry	2,abk,vc	vs	Vfi	eh	m	Vf,f	-
Location 2									
A	5 YR 8/1,w	7.5 YR 7/1, lg	2,m,vc	s	Fi	vh	-	C,m	Clear
AB	5 YR 8/2,pw	7.5 YR 7/1, lg	2,abk,vc	vs	Vfi	vh	f	Vf,f	Abrupt
Bt1	10 YR 7/6, ry	2.5 YR 7/6, lr	2,sbk,c	vs	Efi	eh	m	Vf,vf	Clear
Bt2	10 YR 7/6, ry	7.5 YR 5/6, sb	2,m,vc	vs	Efi	eh	m	Vf,vf	-
Location 3									
A	5 YR 7/1, lg	10 YR 7/3, vpb	2,m,vc	ss	Fi	vh	-	C,m	gradual
AB	10 YR 7/6, ry	10 YR 8/6, y	2,m,vc	vs	Vfi	vh	f	Vf,vf	Clear
Bt1	10 YR 7/8, ry	5 YR 7/8, ry	2,m,vc	vs	Vfi	vh	f	Vf,vf	Abrupt
Bt2	10 YR 8/4, y	5 YR 7/6, y	2,m,vc	Ps	Efi	eh	m	Vf,vf	-

Colour: y = yellow, ry = reddish yellow, w = white, pw = pinkish white, lg = light grey, Lr = light red, sb = strong brown, vpb = very pale brown, pg = pinkish grey. **Mottles:** f = few, m = many; **Structure:** 2 = moderate, Bk = block, M = massive, abk = angular blocky, sbk = subangular blocky, c = coarse, vc = very coarse. **Consistence: S**= sticky. Vs = very sticky, ss = slightly sticky, Ps = slightly plastic, fi = firm, vfi = very firm, efi = extremely firm, vh = very hard, eh = extremely hard, h = hard. **Roots:** C= common, vf = very fine, vf = very few, mf= moderately few, f=fine.

Mottles were absent at the epipedons in all investigated soils, few in the middle or AB horizons and many at the Bt1 and Bt2 horizons in all investigated soils although the Bt1 horizon at location 3 had few mottles. All the pedons had abundant redoximorphic features in form of strong brown mottles due to the reducing/waterlogged soil conditions. Researchers observed similar mottles respectively in subsoils of floodplains in southern Nigeria (Akpan-

Idiok, and Ogbaji, 2013; Obasi et al., 2015a), surface-water grey soils in Bangladesh (Khan *et al.,* 2012) and pedological properties of typical alluvial soils in Tanzania (Asheri et al., 2017).

Soil structure determination indicated that all the investigated soils had moderate structures; structure that is well formed and distinct peds, moderately durable and evident, although not distinct in undisturbed soil. In location 1, structure was blocky and coarse at the epipedon while at the Bt2 horizon it was sub-angular blocky in form and very coarse in its size. At location 2, the structure was massive in form and very coarse in its size at the A and Bt2 horizons. The same trend was observed at the location 3 where all horizons had massive and very coarse structure. This massive structure shows little or no tendency to break apart under light pressure into smaller units. This structure was due to relative presence of clay structure from the shale/alluvium parent material of the study area. This tends to bind the particles together with some sort of strong and cohesive forces which when dry forms coarse to very coarse or massive structure. This results corroborates the reports of Obasi et al., (2015b) who worked on the soil of Otamiri Watershed in Umuagwo-Ohaji in the same agro-ecology.

Soil consistence when wet ranged from sticky in locations 1 and 2 to slightly sticky in location 3 at their surface horizon and from very sticky in locations 1 and 2 to slightly plastic in location 3 at their Bt2 horizons. Consistence when moist ranged from firm to very firm from top to bottom of profile in location 1, firm to extremely firm from top to bottom of the profile in locations 2 and 3. When dry, consistence of the studied soils ranged from very hard to extremely hard from top to bottom in all locations. The stickiness of the consistence when wet reveals the fact that the investigated soils are of shale parent materials under Asu river group. The firmness when moist and hard to extremely hard when dry were as a result of clay properties which exhibited binding properties on the soil particles.

Root abundance indicated that the top (Ap) horizons had common and many roots while AB horizons had moderately few and fine roots at location 1, very few and very fine in locations 2 and 3. All other horizons in all locations ranged from very few and fine to very few and very fine in locations 1, 2 and 3. The roots were more on or near the epipedons of the studied soils. Most of the roots encountered were from the rice plant which decreased down the horizons in all investigated soils.

Horizon boundary attributes varied among and within pedons, whereby distinctness ranged from abrupt to gradual in all investigated soils, but topography was dominantly smooth.

The differentiation of horizons within the pedons was made on soil colour and textural variations similar to that of Orimoloye et al., (2010)**,** implying that the soils are young. The overall, morphology of the studied soils were typical of shale/alluvial soil formation of the Asu river group. This is in line with the study of Asheri et al., (2017) who stated that the morphology and genesis of Tanzanian lowland soils were of alluvia soil formation.

The physical properties of the studied soils are shown in table 2. Soils textural properties indicated that sand and silt had similar trends as they decreased down the profile in all studied locations. While clay took an opposite trend as it increased down the horizons in all locations. Sand had means of 46.24, 41.74 and 46.76%; Silt had means of 25, 28 and 22% while clay had means of 27.54, 27.76 and 26.76% all in locations 1, 2 and 3 respectively. The textural class of the studied soils ranged from sandy loam at the epipedons to clay loam at the endopedons of locations 1 and 2 while location 3 recorded sandy loam in all its horizons.

Table 2: Soil Physical Properties

Location	Depth (cm)	Sand ←	Silt %	→ Clay	Silt/Clay Ratio	TC	BD g/cm^3	Porosity (%)
Pedon 1								
Ap	0 – 15	51.24	28.0	20.76	1.35	SL	1.28	51.69
AB	15 – 37	48.24	27.0	24.76	1.09	SL	1.31	50.56
Bt1	37 – 75	45.24	24.0	28.76	0.83	SL	1.36	48.67
Bt2	75 – 110	40.24	21.0	38.76	0.54	CL	1.42	46.42
Mean		46.24	25.0	27.54	0.95		1.34	49.34
CV		4.1	28.3	7.2	3.93		4.6	Nd
Rank		LV	MV	LV	LV		LV	Nd
Pedon 2								
Ap	0–75	44.24	31.0	24.76	1.25	SL	1.32	50.19
AB	17–43	42.24	30.0	27.76	1.08	SL	1.43	46.04
Bt1	41–83	40.24	27.0	32.76	0.82	CL	1.48	44.15
Bt2	83–124	40.24	24.0	25.76	0.93	CL	1.53	42.26
Mean		41.74	28.0	27.76	1.02		1.44	45.66
CV		4.4	57.7	13.3	4.33		6.2	Nd
Rank		LV	HV	LV	LV		LV	Nd
Pedon 3								
Ap	0–16	50.24	33.0	17.76	1.86	SL	1.20	54.72
AB	16–38	47.24	27.0	25.76	1.05	SL	1.28	51.69
Bt1	38–76	45.24	25.0	29.76	0.84	SL	1.34	49.34
Bt2	76–126	44.24	22.0	33.76	0.65	SL	1.46	44.91
Mean		46.74	26.75	26.76	1.10		1.32	50.17
CV		2.5	55.4	14.1	3.92		8.3	Nd
Rank		LV	HV	LV	LV		LV	Nd

Clay content increased with depth in all pedons providing some indication of clay eluviation-illuviation. Asheri et al.,(2017) observed consistent clay increase with depth as an indication of clay migration in an alluvial soils. Also, the relatively higher clay concentrations at locations 1 and 2 are indications that these areas would retain more moisture compared to location 3 since Kebeny et al., (2015) reported that a pedon with high clay content have higher moisture retention capacity with a gradual moisture decrease as suction potential increased, compared to ones dominated by sand with a rapid decrease in moisture content as the suction potential increased.

Silt-clay ratios decreased down the profile in all investigated locations and scored means of 0.95, 1.02 and 1.10 in locations 1, 2 and 3 respectively. Silt-clay ratio (SCR) is an important criterion used in the evaluation of clay migration, stage of weathering and age of parent material and soil (Yakubu and Ojanuga, 2013). The more highly weathered a soil is, the lower the silt fraction. FAO, (1990) reported that silt-clay ratio less than 0.20 indicates a low degree of weathering. Ayolagha, (2001) on the other hand reported that old parent materials usually have a SCR below 0.15 while SCR above 0.15 is indicative of young parent materials. However, results of this study showed that all the soils had silt-clay ratios above 0.2 indicating a high degree of weathering potentials in all the soils. Higher SCR (0.95, 1.02 and 1.10) recorded in locations 1, 2 and 3 of soils underlain by the Asu river group indicated young parent material.

Bulk density and porosity had an opposite trend as bulk density increased down the profile, porosity decreased down the profile. The means of bulk density were 1.34, 1.44 and 1.32 g/cm^3 while the means of the porosity were 49.34, 45.66 and 50.17 % in locations 1, 2 and 3 respectively. This trend has been observed by Obasi et al., (2015) who worked on the rice soils of the region.

However, Esheri et al., (2017) noted that the decreasing state of bulk density was due to the fact that subsurface layers are more compacted and have less organic matter, aggregation, and root penetration compared to surface layers, leading to less pore spaces. Bulk density therefore affects several processes in the soils including; infiltration, rooting depth, available water capacity, soil porosity, plant nutrient availability, and soil microbial activity, which in turn influence key soil pedogenic processes as well as productivity. USDA-NRCS (2016) suggested that bulk density values greater than 1.65 g/cm3 are unfavorable to root growth in sandy clay loams and clay loams. Thus, the observed bulk density values in Pedons of the studied soils are favorable in that regard.

The results of soil chemical properties of the study site are as shown in the table 3 below. The results indicated that soil pH had no particular trend in some part of the study area. This is because while the trend decreased in locations 1 and 2, it however increased in location 3. Mean pH were 5.25, 5.16 and 5.15 in locations 1, 2 and 3 respectively. Soil pH is one of the most essential chemical properties of the soil and has been rated as follow by Landon (1991); pH (H_2O) of 4.6 - 4.9 as very low, < 5.5 as low and 5.5 to 7.0 as medium. The pH of the studied locations were however low and may be attributed to low amounts of bases caused by leaching during fluctuations of water table and percolation of water during flooding periods, removal of bases through crop harvests and farming practices. The increase of pH down the profile in location 3 is in agreement with Khan et al., 2012 who observed similar trend of pH increasing with depth in annually flooded soils of Bangladesh.

Organic carbon, organic matter and total nitrogen all decreased down the profile recording means of 0.715, 0.571, 0.468%; 1.108, 0.991, 0.568%; 0.068, 0.055, 0.044% for OC, OM and TN in locations 1, 2 and 3 respectively. The decreasing situation of OC, OM and TN down the profile were related and caused by reduction of litter deposits and organic substances down the profile. Available phosphorus increased in the first 3 horizons and decreased in the Bt2 horizon of location 1 while it decreased in the other locations. Available P scored means of 27.68, 24.18 and 20.3 mg/kg in locations 1, 2 and 3 respectively. The phosphorus content of the representative pedons is generally high (>15 mg/kg) based on the rating Tabi et al., (2012) who worked on the Chari flood plain of Cameroun. Researchers such as Enwezor et al., (1990); Adepetu, (2000) corroborated this by stating that available P <15 mg/kg was low for Nigerian soils. Uzoho et al., (2004) believed high acidity (pH < 5.0) usually leads to low soil available P as P gets fixed in high acidic soils. However, the studied soils had pH > 5.0 < 5.5 which though not optimum pH (5.5 – 7.0) for good crop growth and sustenance leading to a medium to high P content of the studied soils.

Table 3: Chemical Properties of Studied Soils

Location	Depth	pH	OC	OM	TN	C/N	Avail.P	Ca	Mg	K	Na^+	H^+	Al^{3+}	TEA	TEB	ECEC	B. Sat	Al Sat
	(cm)			%		Ratio	mg/kg					Cmol/kg					%	%
Pedons 1																		
A	0–15	5.55	1.084	1.876	0.103	10.52	28.3	1.86	0.93	0.079	0.056	0.53	trace	0.53	2.925	3.455	84.66	5.00
AB	1 –37	5.28	0.963	1.660	0.091	10.58	30.6	1.72	1.08	0.194	0.062	0.46	0.50	0.96	3.056	4.016	76.10	12.45
B ti	37–75	5.12	0.506	0.872	0.048	10.54	32.3	1.63	0.93	0.173	0.053	0.56	0.44	1	2.786	3.786	73.59	11.62
Bt2	75–110	5.08	0.308	0.531	0.029	10.62	19.5	1.96	0.71	0.162	0.051	0.71	trace	0.71	2.883	3.593	80.24	5.00
Mean		5.25	0.715	1.108	0.068	10.57	27.68	1.79	0.91	0.152	0.055	0.57	0.24	0.8	2.913	3.713	78.65	8.52
Cv		4.1	51.5	45.1	51.7	Nd	20.6	8.2	16.7	33.2	133.1	18.6	115.	27.6	3.8	6.6	6.2	Nd
Rank		LV	HV	HV	HV	Nd	MV	LV	MV	MV	HV	MV		MV	LV	LV	LV	Nd
Pedon 2																		
A	0–75	5.19	0.835	1.440	0.079	10.56	29.8	1.03	0.57	0.098	0.033	1.02	trace	1.02	1.731	2.751	62.92	5.00
AB	17–43	5.22	0.621	1.071	0.059	10.52	26.9	1.22	1.26	0.083	0.046	0.51	0.96	1.47	2.609	4.079	64.00	23.53
Bti	41–83	5.09	0.510	0.879	0.048	10.62	21.8	1.36	0.78	0.073	0.051	0.32	0.33	0.65	2.354	3.004	78.40	10.98
Bt2	83–124	5.12	0.352	0.607	0.033	10.66	18.2	0.95	1.01	0.062	0.056	0.65	0.69	1.34	2.078	3.418	60.80	20.19
Mean		5.16	0.571	0.991	0.055	10.59	24.18	1.14	0.82	0.079	0.046	0.63	0.41	1.12	2.193	3.313	66.50	14.93
Cv		1.2	35.0	35.0	35.4	Nd	21.4	16.3	16.7	19.4	21.3	47.4	84.5	32.7	17.2	17.5	12.1	Nd
Rank		LV	MV	MV	HV	Nd	MV	MV	MV	MV	MV	HV	HV	MV	MV	MV	LV	Nd
Pedon 3																		
A	0–16	5.06	0.615	1.060	0.058	10.60	22.5	0.91	6.63	0.086	0.063	0.44	0.71	1.15	1.759	2.909	60.50	24.41
AB	16–38	5.20	0.482	0.833	0.046	10.47	17.5	1.27	0.78	0.071	0.052	0.63	0.56	1.19	2.173	3.363	64.60	16.65
Bt1	38–76	5.22	0.409	0.705	0.038	10.76	19.8	1.32	0.88	0.097	0.043	0.69	0.43	1.12	2.34	3.46	67.60	12.43
Bt2	76–126	5.10	0.365	0.629	0.035	10.42	21.3	1.49	1.0	0.053	0.037	0.48	0.38	0.86	2.58	3.44	75.00	11.05
Mean		5.15	0.468	0.568	0.044	10.56	20.3	1.25	2.32	0.077	0.049	0.56	0.52	1.08	2.213	3.293	66.90	10.40
Cv		1.5	23.4	23.4	23.2	Nd	10.6	16.8	31.0	24.9	23.2	21.3	28.4	13.8	15.6	7.9	9.1	Nd
Rank		LV	MV	MV	MV	Nd	LV	MV	MV	MV	MV	MV	MV	LV	MV	LV	LV	Nd

OC = organic carbon, OM = organic matter, TN = total nitrogen, Av.P = available phosphorus, TEB = total exchangeable bases, TEA = total exchangeable acidity, ECEC = effective cation exchange capacity, B. Sat = base saturation, Al Sat. = aluminum saturation, CV= Coefficient of Variation, LV= Low variability, MV= Moderate variability, HV= High Variability.

Calcium had no particular trend in locations 1 as it tends to be highest in Bt2 horizon. It however increased progressively in location 2 although it dropped to the lowest at Bt2 horizon whereas it increased all through down the profile across all horizons in location 3. Ca had means of 1.79, 1.14 and 1.25 cmol/kg in locations 1, 2 and 3 progressively. The Ca content of the soils were very low (<2 Cmol/kg) according to Tabi et al., 2012) in all investigated pedons.

Magnesium had no particular in all locations and recorded high accumulation at the surface horizon of location 3. The means Mg were 0.91, 0.82 and 2.32 in locations 1, 2 and 3 respectively. Mg contents of locations 1 and 2 were low (0.5 – 1.5 cmol+/kg) while location 3 was medium (1.5 – 3.0 cmol+/kg). Potassium and Sodium did not have definite trend in location 1 while K also had no definite trend in location 3. However, K and Na decreased consistently in pedon 2 and Na in pedon 3. Means of K and Na were 0.152, 0.079, 0.077; 0.055, 0.046, 0.049 cmol/kg in locations 1, 2, and 3 respectively. Location 1 was low (0.1 – 0.3 cmol+/kg) in K scoring 0.152 cmol+/kg. All other locations were very low in K (<0.1 cmol+/kg). All investigated locations were very low in Na being <0.1 cmol+/kg according to Tabi et al., (2012).

Total exchangeable acidity (TEA) was low compared to their total exchangeable bases (TEB) counterparts in all the investigated soils. Their means were 0.8, 1.12, 1.08; 2.91, 2.19, 2.21 cmol/kg for TEA and TEB at locations 1, 2 and 3 respectively. As a result the base saturation was moderate to optimum in the investigated soils compared to the Al saturation which was quite low. Mean base saturation and Al saturation were; 78.65, 66.50, 66.90%; 8.52, 14.93, 10.40% in locations 1, 2 and 3 respectively. This situation therefore suggests that Al toxicity may not be a challenge to the dominant crops grown on the investigated soils. Msanya et al., (2001) suggested that soils with BS > 50% are fertile soils and vice versa although the following classes were recognized: BS < 20% as low, 20-60 as medium, and above 60% as high.

Taxonomic Classification

The diagnostic criteria for classification of soils of Ohaozara according to the USDA Soil Taxonomy (Soil Survey Staff, 2010) include an udic soil moisture regime and a hyperthermic soil temperature regime characteristic of semi-arid to sub-humid subtropical climate. The investigated soils have their silt/clay ratios as <1.0 in location 1, and > 1.0 in locations 2 and 3, suggesting that the investigated soils were mostly young soils such as Inceptisol or Entisol. There was consistent clay increase in all studied soils leading to formation of argillic horizon in Bt1 horizon of location 2 and kandic horizons in locations 1 and 3. Organic matter contents and stratification qualified pedons in locations 1, 2 and 3 as Fluvents, since there was an irregular decrease in organic-carbon content (Holocene age) between a depth of 25 cm and either a depth of 125 cm below the mineral soil surface. Isohyperthermic soil temperature regime placed the investigated soils on the suborder Tropepts, The temperature regime and percentage base saturation were considered at the subgroup level in the soil taxonomy. A base saturation (by NH4OAc) of more than 60 percent or more at a depth between 25 and 75 cm from the mineral soil surface. There was presence of lithic contact in location 1, at a depth of 110 cm while water was encountered in locations 2 and 3 at a depth of 124 and 126 cm respectively.

Therefore, pedon 1 is classified as **Typic Eutrudept (USDA) and Eutric Cambisols (WRB)** while pedons 2 and 3 were classified as **Aquic Eutrudepts (USDA) and Gleyic Leptosols (WRB)**.

Conclusion

The parent material is Shale/Alluvium derived from Asu River group. The profiles were deep enough for rice cultivation and drainage indicated well drained for Ap and AB horizons and poorly drained for Bt1and Bt2 horizons. Soils textural properties indicated that sand and silt had similar trends as they decreased down the profile in all studied locations. While clay took an opposite trend as it increased down the horizons in all locations. Therefore, pedon 1 is classified as Typic Eutrudept (USDA) and Eutric Cambisols (WRB) while pedons 2 and 3 were classified as Aquic Eutrudepts (USDA) and Gleyic Leptosols (WRB).

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Radioactivity of Drinking Waters from Different Regions of Bulgaria in the Period 2017-2019

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Abstract

Radioactivity of drinking waters is determined by trace quantities of natural radionuclides ^{238}U, ^{232}Th, their daughter products and ^{40}K. They are transferred to water by processes of erosion and dissolution of aquifer rocks and minerals. Man-made radionuclides may also occur in water as a result of technological pollution.

Therefore, annual radiological monitoring is a key factor in ensuring water safety.

In the present study, radiological monitoring of drinking waters from different regions in Bulgaria was carried out according to the national regulations in the period 2017-2019. Content of natural uranium, gross alpha and beta activity, radon-222 and tritium in water samples were determined.

Content of radiological indicators under study was not exceeding the reference values in the predominant part of analyzed samples. Relatively higher values of natural uranium and gross alpha activity were observed in insignificant number of samples, probably due to specific hydro-geological characteristics of the aquifers in the respective regions, as well to the presence of closed uranium mining sites near them. Content of radon and tritium in all tested waters were below the parametric values.

As a result of the present survey it can be concluded that drinking waters in the studied regions were not hazardous for human health from radiological point of view.

Keywords: radioactivity of waters, U, gross alpha and gross beta activity, ^{222}Rn, ^{3}H

Introduction

Radioactivity of waters is determined by the normal presence of natural radionuclides ^{238}U, ^{232}Th, their daughter products and ^{40}K. They are transferred to waters by processes of erosion and dissolution of rocks and minerals formed in aquifers. Uranium mining and processing, coal mining and operation of thermal power plants, production and use of mineral fertilizers can lead to man-made intensification of local radiation background and increase in content of natural radionuclides in water (Carvalho et al., 2014, Yordanova et al., 2011, Chalupnik et al. 2001, Azoazi et al., 2001). Man-made radionuclides may also be present in water as a result of technological processes. Therefore, the regular radiological monitoring is a key factor in ensuring drinking water safety.

The aim of the present study was to determine the content of natural uranium, gross alpha and beta activity, ^{222}Rn and ^{3}H in waters from different regions in Bulgaria for the period 2017-2019. Monitoring of the main radiological indicators was carried out in accordance with regulations set in the national legislation (Table 1 and Table 2) (Regulation No. 9, 2001).

Table 1. *Parametric values for radon, tritium and Total Indicative Dose (TID) in water for drinking and household purposes.*

Indicator	**Parametric value**	**Unit**
Radon	100	Bq/l
Tritium	100	Bq/l
Total Indicative Dose	0,1	mSv

Table 2. Reference level of gross alpha and beta activity

Indicator	**Reference level**	**Unit**
Gross alpha activity	0,1	Bq/l
Gross beta activity	1,0	Bq/l

Materials and Methods

Testing Laboratory of Radioecology and Radioisotope Research at ISSAPP "Nikola Pushkarov" is accredited for determining content of radioactive elements in water, soil, plants, food and food products under BDS EN ISO/IEC 17025:2018.

1040 water samples were analyzed for the period 2017 - 2019.

Content of natural uranium was determined by a method based on formation of tetravalent uranium complex with arsenase III and spectrophotometric measurement of the samples at 655 nm wavelength.

Gross alpha and gross beta activity were determined according to BDS EN ISO 9696/2017 and ISO 9697/2019 respectively. Planchets with dry residue of aliquot part of water samples were prepared and measured by low-background gas proportional alpha/beta counter.

Radon-222 was determined by gamma spectrometry by the line of ^{214}Bi at 609 kV . A DSA 1000 multi-channel analyzer, product of CANBERRA with pure Ge detector, 30% efficiency and 1.8 keV resolution, was used (Naidenov et al.).

Determination of tritium in water samples was carried out according to a method for liquid scintillation counting [Naidenov et al.].

The results are validated by annual participations in interlaboratory comparisons, proficiency test schemes and regular internal quality control.

Results and Discussion

1. *Natural uranium, gross alpha and beta activity in water samples*

Natural uranium is a mixture of three isotopes - ^{238}U, ^{234}U and ^{235}U. In addition to being radioactive, it is also toxic as chemical element and its ingestion can lead to kidney damage. Maximum permissible concentration of uranium in drinking water under Bulgarian regulations is 0.03 mg/l. The number of water samples with relatively higher uranium content are presented on Fig. 1.

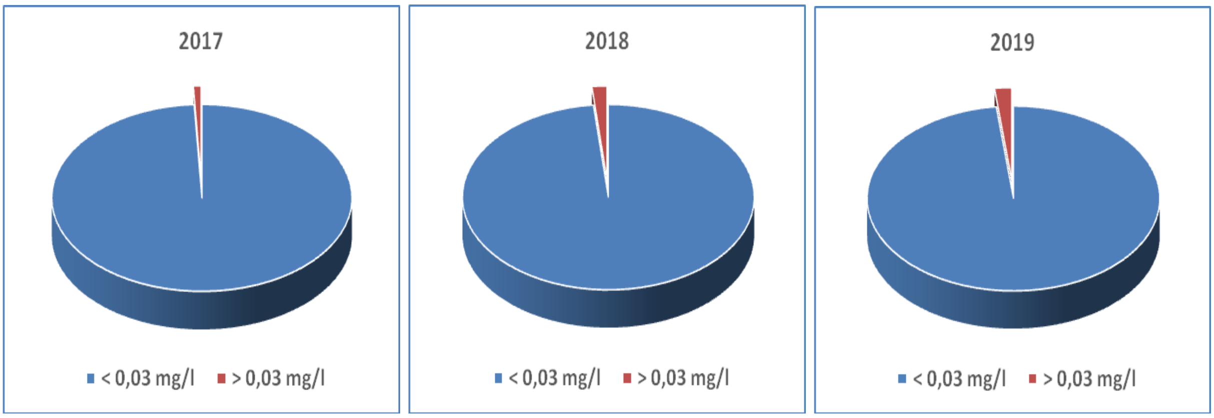

Fig. 1. *Number of the samples with increased content of natural uranium per year.*

The percentage of waters with increased content of natural uranium for the three years period was 1%.

Gross alpha activity in water is mainly due to uranium isotopes (^{238}U, ^{234}U, ^{235}U) and ^{226}Ra. Beta activity is usually due to a large extent to ^{40}K and short-lived beta emitters of the ^{238}U family. Determination of gross alpha and beta activity is a relatively fast and effective method for preliminary screening of water. The reference levels specified in Regulation 9 for gross alpha and beta activity are 0.1 Bq/l and 1 Bq/l, respectively. If they are not exceeded it is assumed that the Total Indicative Dose (TID) is under the reference level of 0,1 mSv/year set in the regulations.

Results of gross alpha activity measurements in water samples are presented in Fig. 2.

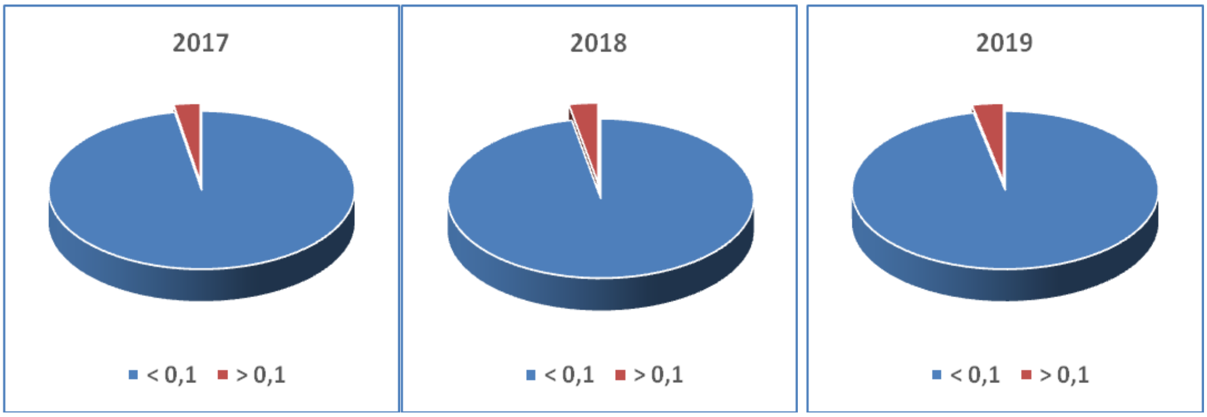

Fig. 2. *Number of the samples with increased content of gross alpha activity from the total number of tested samples per year.*

Increased gross alpha activity was found in 3 % of all waters tested in the period 2017 - 2019. The data for gross beta activity in all samples were below the reference level of 1 Bq/l.

According to the regulations, if gross alpha activity exceeds the screening level of 0.1 Bq/l, content of individual radionuclides should be determined and Total Indicative Dose calculated. Further analysis of data found the increased gross alpha activity in the samples was entirely due to the contribution of uranium. In general uranium chemical toxicity is much more marked than its radiotoxicity (Rump et al., 2019). Radium, which is much more radiotoxic, has a relatively low solubility in water and does not form soluble complexes. Uranium isotopes (^{234}U and ^{238}U) are generally the most common radionuclides in water. Uranium forms soluble stable complexes (e.g. carbonates) under oxidative conditions and can migrate on long distances (Nuccetelli et al., 2012). Total Indicative dose (TID) was calculated with the respective uranium concentrations and uranium dose coefficient (Eckerman et al., 2012). It was below the parametric value in all cases and the waters were considered safe for human health.

Comparison of results of radiological indicators in waters from different regions in Bulgaria obtained in the years, showed the number of samples with increased content of uranium and gross alpha activity raised upon entry into force of more conservative reference values for natural uranium (twice lower) and gross alpha activity (five times lower) in Bulgarian legislation.

Waters with relatively high uranium concentrations were from the regions around Plovdiv, Rakovski, Haskovo and Burgas and those with increased gross alpha activity from regions around Burgas, Plovdiv, Rakovski, Haskovo, Petrich, Dobrich, Vratsa and Tran.

Higher concentration of uranium in waters from these regions may be explained with the specific hydro-geological characteristics of the aquifers and the presence of rocks like granites, gneisses and schists containing higher quantities of natural uranium. Another reason could be the former uranium mining and processing carried out on sites in the regions in the past.

2. ^{222}Rn activity concentration in water samples

The world average annual effective dose obtained from external and internal exposure to the natural radiation background is 2.4 mSv/y. 50% of it is due to the inhalation of radon and its short-lived daughter products contained in atmosphere (Brenner, 1994). 98% of human internal exposure is result of the inhalation of radon daughter products retaining in the body and affecting bronchial epithelium in lungs, and only 2% are due to radon (radon-222) itself.

Although radiation risk of radon exposure through water consumption is much lower than the caused by indoor radon inhalation, European legislation and the relevant Regulation 9 have set a parametric value of 100 Bq/l for the radionuclide in drinking water. Corrective action shall be taken in all cases where radon activity concentration exceeds 1000 Bq/l to provide radiation protection.

Radon-222 content was measured in 300 drinking water samples. All results were under the parametric value, the predominant part of them being below the minimum detectable activity (MDA) of the measurement (10 Bq/l). Activity concentration over MDA was determined in 63 samples (Table. 1).

Table 3. *^{222}Rn activity concentration in water samples [Bq/l]*

	Sampling site	^{222}Rn, Bq/kg
1	Burgas District, Vratitsa	25±5
2	Burgas District, Detelina	25±5
3	Burgas District, Dimchevo	15±10
4	Burgas District, Dobrinovo	30±10
5	Burgas District, Zhytosvyat	50±5
6	Burgas District, Krumovo gradishte	25±3
7	Burgas District, Lesnovo	20±5
8	Burgas District, Livada	16±5
9	Burgas District, Pirene	20±5
10	Burgas District, Pchelin-1	40±4
11	Burgas District, Pchelin-2	75±7

Table 3. ^{222}*Rn activity concentration in water samples [Bq/l] (continue)*

12	Burgas District, Raklinovo	20±5
13	Burgas District, Raklitsa	25±5
14	Burgas District, Sinyo Kamene - 1	30±3
15	Burgas District, Sinyo Kamene - 2	25±3
16	Burgas District, Sinyo Kamene village -3	45±10
17	Burgas District, Sinyo Kamene -4	25±10
18	Burgas District, Sinyo Kamene village-5	25±10
19	Burgas District, Sadievo	35±10
20	Burgas District, Troyanovo	80±8
21	Burgas District, Trastikovo	25±5
22	Burgas District, Chukarka , zone 1	50±10
23	Burgas District, Chukarka, zone 2	20±5
24	Burgas District, Zheleznik	30±3
25	Veliko Tarnovo District, Elena	25±3
26	Veliko Tarnovo District, Pavlikeni	30±3
27	Veliko Tarnovo District, Suhindol	30±3
28	Veliko Tarnovo District, Byala Cherkva,	15±3
29	Veliko Tarnovo District, Visovgrad	20±5
30	Veliko Tarnovo District, Delyanovtsi	20±5
31	Veliko Tarnovo District, Karaisen	30±3
32	Veliko Tarnovo District, Koevtsi	30±3
33	Veliko Tarnovo District, Krumchevtsi	30±3
34	Veliko Tarnovo District, Mihaltsi	30±3
35	Veliko Tarnovo District, Novachkini	30±3
36	Veliko Tarnovo District, Ovcha Mogila	30±3
37	Veliko Tarnovo District, Ovcha Mogila	70±6
38	Veliko Tarnovo District, Rusalya	25±5
39	Veliko Tarnovo District, Stefan Stambolovo	25±5
40	Veliko Tarnovo District, Hotnitsa	40±4
41	Veliko Tarnovo District, Hanevtsi	70±7
42	Veliko Tarnovo District, Chervena	20±3
43	Dobrich District, Dobrich, catchment	30±3
44	Dobrich District, Dobrich	70±7
45	Montana District, Montana	30±10
46	Montana District, Boychinovtsi	30±10
47	Montana District, Vladimirovo	25±8
48	Pernik District, Trun Municipality, Brul	70±15
49	Pernik District, Trun Municipality, Glogovitsa	50±10
50	Pleven District, Kneja	30±10
51	Plovdiv District, Katunitsa	50±10
52	Plovdiv District, Kosovo	50±5
53	Plovdiv District, Markovo	20±8
54	Razgrad District, Ezerche	25±3

Table 3. *^{222}Rn activity concentration in water samples [Bq/l] (continue)*

55	Razgrad District, Kamenar	20±3
56	Razgrad District, Kostandenets	25±3
57	Razgrad District, Malak Porovets,	30±5
58	Razgrad District, Staro Selishte	25±5
59	Silistra District, Vodno Dulovo	65±6
60	Silistra District, Staro Selo	45±9
61	Sofia District, Dolna Banya	40±10
62	Sofia District, Kremikovtsi	40±10
63	Stara Zagora District, Kazanlak	25±5

Radon content in drinking waters may vary widely. For comparison, in some European countries the following ^{222}Rn activity concentrations were determined in Bq/l: Austria - 1.46-644 (Wallner and Steininger, 2007), Germany - <1.3-1800 (Beyerman et al., 2010), Portugal - 1.12-112.77 (Lopes et al., 2005), Greece - 0.23-24 (Nikolopoulos et al., 2008).

3. Tritium content in waters from different regions of the country

Tritium is a cosmogenic radionuclide that forms in the upper atmosphere. It occurs in rainwater in the form of treated water (HTO) with activity concentration of about 5 Bq/l. Tritium has low radiotoxicity. Its dose coefficient is three to four orders of magnitude lower than the coefficients of natural chain radionuclides.

Natural levels of ^{3}H in environment increased in result of nuclear weapon tests carried out from 1945 to 1963. Another source of tritium are nuclear power plants (NPPs), as ^{3}H is produced as a by-product of uranium fission. Tritium contamination around NPPs is mainly found in nearby surface waters (Querfeld et al., 2019).

The parametric value set for tritium in Regulation 9 is 100 Bq/l. Elevated levels of tritium may by indicative for the presence of other artificial radionuclides and if ^{3}H activity concentration exceeds the parametric value, an analysis for other artificial radionuclides is required.

^{3}H content was determined in 423 water samples in the three years period. Tritium activity concentration in all samples was lower than the parametric value within the range <3 ÷ <20 Bq/l. in 80% of the samples the values were below the minimum detectable activity of 3 Bq/l. No technological contamination with tritium was found.

Conclusion

In the predominant part of analysed samples radiological indicators under under monitoring did not exceed the values set in the regulations.

Relatively higher values of natural uranium and gross alpha activity were observed in minimal number of samples. They could be probably explained both by the specific hydro-geological characteristics of aquifers in the observed regions and by sites of closed uranium mining and processing near them.

Increased gross alpha activity in the samples was found to be due to the contribution of natural uranium. Total Indicative dose (TID) was calculated with the respective uranium concentrations and uranium dose coefficient. It was below the parametric value in all cases and the waters were considered safe for human consumption.

The measurements of ^{3}H content in waters did not indicate any technological contamination in result of uncontrolled leakage of the radionuclide in studied waters.

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Effects of Pig and Goat Droppings on Soil Physiochemical Properties and Yield of Cucumber (*Cucumis sativus L.*)

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Abstract

This study was carried out at the teaching and research farm of the Department of Crop Production and Horticulture, Lagos State Polytechnic Ikorodu to determine the effects of different levels of goat and pig droppings on the performance of cucumber (Cucumis sativus). The experiment was laid out in Randomized Complete Block Design with five experimental treatments replicated three times. The treatments applied were goat droppings at 5 and 10 tonnes per hectare, pig droppings at 5 and 10 tonnes per hectare and control 0 tonne per hectare. Data collected were vine length (cm), vine girth (cm) number of leaves, number of branches, and days to 50% flowering, weight of fruit (kg), number of fruits, length of fruit (cm) and width of fruits (cm). The results from the data analysis indicated that number of branches of cucumber, its length and diameter were significantly affected by the different rates of application of goat and pig droppings. Based on the outcome of this study, 5 tonnes per hectare of goat manure should actually be adopted for farmers in Ikorodu Local Government Area of Lagos State. However, further research should be carried out to determine the rate of manure suitable for the optimum yield of cucumber (Cucumis sativus). Farmers are advised to use more tonnes of manure at a higher rate to improve soil physio-chemical properties and to enhance crop growth and yield.

Keywords: Pig droppings, Goat dropping, soil physiological properties, yield, cucumber

Introduction

Cucumis sativus is a widely cultivated plant in the gourd family, Cucurbitaceae. It is a creeping vine that bears cucumiform fruits that are used as vegetables. There are three main varieties of cucumber: slicing, pickling, and seedless. Within these varieties, several cultivars have been created. The cucumber is originally from South Asia, but now grows on most continents. Many different types of cucumber are traded on the global market (Nonneck, 1989; Wells, 2016).

The cucumber is a creeping vine that roots in the ground up trellises or other supporting frames, wrapping around supports with thin, spiraling tendrils. The plant may also root in a soilless medium and will prowl along the ground. The vine has large leaves that form a canopy over the fruits. The fruit is roughly cylindrical, but elongated with tapered ends, and may be as large as 60 centimetres (24 in) long and 10 centimetres (3.9 in) in diameter.

Cucumber fruit consist of 95% water. They are vine crops and grown on the ground or on poles or trellises to suspend to fruit (Nonneck, 1989; Wells, 2016) Cucumbers come in three different types: seedless, seeded, and mini. The soils where cucumber is cultivated require moderate to high nutrient levels so as to achieve high yields. Infertile soils result in bitter and misshapen fruits which are often rejected by consumers thereby reducing farmers' income. (Jannick *et al*., 2007).

Production of cucumber in Nigeria has increased probably due to awareness being created by its market demand and economic returns, short duration in maturity or due to its nutritional and medicinal values. Hence it has become a popular vegetable crop in Nigeria. Both older and young people enjoy the cucumber fruit of which many in their leisure time usually eat with fried groundnut in their offices, homes, and market place or recreational areas. This crop required high amount of soil nutrients from seedling stage to maturity and highly sensitive to excessive water or water-logs environment and adequate soil tillage for easy fragile root penetration, is required prior to sowing or planting (Nweke *et al*., 2014).

Nigeria soil has high potential for crop production but yields levels obtained under farmer's condition are usually low due to poor soil management and conservation method, because of problems associated with the use of chemical fertilizers as its scarcity, high cost, ineffectiveness due to blanket use, soil acidity, nutrients, hence the use of Organic Fertilizers to solve all these problems. This necessitates the need to carry out research for good and economical soil management practices in other to improve the soil condition and reduce harm caused by the use of inorganic fertilizers thereby increasing the productivity of arable land. The main objective of this study is to determine the effect of variable rates of pig and goat droppings on the soil physiochemical properties and yield of cucumber (*Cucumis sativus*).

Materials and Methods

Experimental location, land preparation, experimental design and treatments

The experiment was carried out at the Teaching and Research Farms of Lagos State Polytechnic, Ikorodu, Lagos State Nigeria. The experimental site has been under continuous cultivation for over three years without any forms soil amendments. The land was ploughed and harrowed to a fine tilt using a disc plough and harrow.

The experiment was laid out in Randomized Complete Block Design (RCBD**)** because of the heterogeneity of soil at the experimental location. The experiment was carried out on a total area of land measuring 100.8m^2 which was divided into 3 blocks of 18m x 1.2m (2.6m^2), each plot size is 1.2m x 3m (3.6m^2) with a discard of 0.5m to give a total number of 15 plots.

Pig and goat droppings were obtained from nearby farm (Farm Settlement Odogunyan, Ikorodu, Lagos State). The droppings were cured and applied two weeks before planting to allow for mineralization (Eifediyi and Remison, 2010).

Five (5) treatments was used throughout the study which are; Goat droppings(5 and 10 tons ha^{-1}), pig droppings(5 and 10 tons ha^{-1}) and the control plot, which were replicated three times. In addition, the goat droppings and pig droppings were applied to the plots two weeks before planting by broadcasting method.

Crop establishment and maintenance

Cucumber seeds was obtained from agro-allied store Sabo market Ikorodu, Lagos State. Planting was done directly on the main field at a spacing of 60cm x 75cm (Chude etal., 2004) at two seeds per hole then thinned to one stand each at one week after planting and transplanting was also done to supply missing stands to give a total of 8 plants per plot and a total of 120 plants. Manual weeding was carried out on a weekly basis with the use of hoe, which was due to the high grasses infestation and the high rains during the course of the project. Spraying of insecticides and fungicide was done at biweekly intervals to ensure effective chemical control of insects and fungi attacks at seedling stage.

Soil sampling, preparation and Analysis

The soil of the experimental site was analyzed twice, the first one before planting (pre-planting soil analysis) and the second after harvesting (post- planting soil analysis). Soil sample from the top soil 0-20 cm were randomly collected with soil auger from the experiment site for laboratory analysis.. The samples for the experiment were composited, air dried, ground and sieved to pass through a 2mm sieve. The soil sample was analyzed for soil texture, pH, organic carbon, organic matter, total N, exchangeable p, and Exchangeable levels of Ca, Mg, k, Na, Fe, Cu, Mn, Zn, and cation exchange capacity. The two types of manure samples were air dried for and ground to pass through 2mm sieve. The samples were then applied to the plot

Harvesting

Matured fruits were selected for harvest at seven weeks after planting. Harvesting was done by carefully cutting the fruits free from the stalk with the use of sharp knife. The harvested fruits were then taken for data collection.

Data collection and Statistical Analysis

Four (4) plant stands was randomly sampled and tagged per plot for data collection. Data that were collected include:

Growth Parameters; number of leaves. vine length (cm), and number of branches. Yield Parameters; number of days to 50% flowering, number of fruits per plot, length of the fruits (cm), fruits diameter (mm), weight of fruits per plot (kg).

Data collected were subjected to Analysis of Variance (ANOVA), and means of treatments were compared using Duncan Multiple Range Test (DMRT) at 5% level of probability using SAS (version 9.4).

Results

Effect of goat and pig droppings on number of leaves of *Cucumis sativus*

Table 4.1 showed that the number of leaves of cucumber was not significantly affected by different rate of application of goat and pig droppings at 5% level of significance.

At 2 WAP, the highest mean number of leaves (4.83) was observed from *Cucumis sativus* grown with 10tons/ha of pig droppings. However, at 4 WAP the highest mean number of leaves (14.11) was observed from *Cucumis sativus* grown with 10 tons/ha of goat dropping. Meanwhile, at 6 WAP the least mean number of leaves (19.67) was observed from Cucumis sativa grown without manure application (control 0 ton/Ha).

Effect of goat and pig droppings on vine girth (cm) of *Cucumis sativus*

Table 4.1 revealed that at 2 WAP, the thickest stem girth of 0.87 cm was achieved with 5 tons/ha of pig droppings, while the thinnest stem girth of 0.21cm was observed from *Cucumis sativus* grown without manure application (control 0 ton/ha). Whereas, at 4 WAP the thickest stem girth of 0.72 cm was 1.19 obtained from *Cucumis sativus* grown with 10 tons/ha of pig droppings. However, at 6 WAP the thickest stem girth of 1.19cm was also obtained from *Cucumis sativus* grown with 10 tons/ha of pig dropping.

Effect of goat and pig droppings on number of branches of *Cucumis sativus*

Table 4.1, revealed that at 4 WAP the treatments means were significantly different from one another, where the highest mean value of branches (10.58) was produced by *Cucumis sativus* grown with no manure goat droppings while the least was observed from *Cucumis sativus* grown with pig droppings of 5 tons/ha of 5tons/ha and it was also observed that *Cucumis sativus* grown with goat droppings at 5tons/ha had same mean value (8.0) with *Cucumis sativus* grown with 10 tons/ha of pig droppings. However, at 6 WAP *Cucumis sativus* grown without manure application (control 0 ton/ha) had the highest (19.5) number of branches when compare to *Cucumis sativus* grown with 10 tons/ha of pig droppings (16.0) and *Cucumis sativus* grown with goat droppings of 10 tons/ha (13.89).

Effect of goat and pig droppings on vine length (cm) of *Cucumis sativus*

From table 4.1, the vine length of cucumber was not significantly affected by different rate of application of goat and pig droppings at 5% level of significance.

At 4 WAP the longest vine of 12.21 cm was obtained from Cucumis sativa grown with Goat droppings 10 tons/ha and it was observed that *Cucumis sativus* grown with goat dropping of 5 tons/ha and pig droppings of 10 tons/ha had same mean value of 11.58 cm while the shortest vine length (8.00) was obtained from *Cucumis sativus* grown without manure application (control 0 tons/ha). At 6WAP the longest vines (22.20) was observed from *Cucumis sativus* grown without manure application (control 0 tons/ha).

Effect of goat and pig droppings on days to 50% flowering of *Cucumis sativus*

Table 4.2, the different rate of application of goat and pig droppings at 5% level of significance has no significant effect of 50 days to flowering. *Cucumis sativus* grown with Goat droppings at 5tons/ha had the highest (35.58) days to 50%flowering while the least days (32.17) was obtained from *Cucumis sativus* grown with Goat droppings at 10 tons/ha.

Effect of goat and pig droppings on number of fruits of *Cucumis sativus*

According table 4.5, Cucumber grown with 5 tonnes/ha of goat droppings significantly produced the highest fruits with mean value of 8.10 than 7.47 mean number of fruits obtained from Cucumber grown with 10 tonnes/ha of goat droppings which was also significantly different from Cucumber grown with 5 tonnes/ha of pig droppings (7.22), 10 tons/ha of pig droppings (7.15) and 6.41 mean number of fruits obtained from Cucumber grown with no manure application.

Effect of goat and pig droppings on fruits length (cm) of *Cucumis sativus*

From table 4.5, the application rate of goat and pig droppings had no significant effect on the fruit length of cucumber. Cucumber grown with 5 tonnes/ha of goat droppings produced the longest fruits with mean value of 19.78 cm, followed by 19.45 cm mean fruit length obtained from cucumber grown with 5 tonnes/ha of goat droppings while the shortest fruit with mean value of 12.72 cm was obtained from cucumber grown without manure application.

Effect of goat and pig droppings on fruits diameter (cm) of *Cucumis sativus*

According to table 4.5, Cucumber grown with 5 tonnes/ha of goat droppings produced the fattest fruit with mean value of 23.55cm, followed by 20.40 cm mean fruit width obtained from Cucumber grown with 10tonnes/ha of goat droppings which was significantly different from 5.74 cm, 15.14 cm and 3.96 cm mean fruit width obtained from Cucumber grown with 5 tonnes of pig droppings, followed by Cucumber grown with 10 tonnes of pig droppings and Cucumber grown without manure application.

Table 4.1. *Effect of goat and pig droppings on growth of Cucumis sativus at 2 weeks after planting (WAP).*

Manure Types and Quantity	No. of leaves	Vine girth (cm)
5 tons/ha Goat dropping	1.83	0. 28
10 tons/ha Goat dropping	3.42	0.29
5tons/ha Pig dropping	4.75	0.87
10 tons/ha Pig dropping	4.83	0.29
Zero manure application	4.33	0.21
	ns	ns

Table 4.2. *Effect of goat and pig droppings on growth of Cucumis sativus over the period of 4 weeks after planting (WAP).*

Manure Types and Quantity	No. of leaves	Stem girth (cm)	No. of branches	Vine length (cm)
5 tons/ha Goat dropping	13.25	0.62	8.00ab	11.58
10 tons/ha Goat dropping	14.11	0.65	6.94ab	12.21
5tons/ha Pig dropping	11.33	0.61	5.50b	9.88
10 tons/ha Pig dropping	12.17	0.72	8.00ab	11.58
Zero manure application	9.750	0.59	10.58a	8.00

Values represent treatment means. Means were separated using Duncan multiple range test and means within a column followed by different letters are significantly different at P≤0.05.

Effect of goat and pig droppings on fruits yield (kg) of *Cucumis sativus*

From table 4.5, the fruits weights of cucumber were not significantly affected by different rate of application of goat and pig droppings at 5% level of significance. Cucumber grown with 5 tons/ha of goat droppings produced the highest fruits weight of 0.67 kg/plot while least fruits weight with mean value of 0.40 kg/plot was obtained from Cucumber grown without manure application.

Table 4.3. *Effect of goat and pig droppings on growth of Cucumis sativus over the period of 6 weeks after planting (WAP).*

Manure Types and Quantity	No. of leaves	vine girth (cm)	No. of branches	Vine length (cm)
5 tons/ha Goat dropping	45.42	1.17	12.25b	15.68
10 tons/ha Goat dropping	25.03	1.03	13.89ab	12.61
5tons/ha Pig dropping	20.67	1.11	11.00ab	12.10
10 tons/ha Pig dropping	22.17	1.19	16.00ab	12.50
Zero manure application	19.67	1.09	19.50a	22.20

Values represent treatment means. Means were separated using Duncan multiple range test and means within a column followed by different letters are significantly different at P≤0.05.

Table 4.4. *Effect of goat and pig droppings on yield component Cucumis sativus (L).*

	Number of days to 50% flowering	NF	FL (cm)	FD (mm)	FW (kg/ plot)
5 tons/ha Goat dropping	35.58	8.10	19.78	23.55	0.67
10 tons/ha Goat dropping	32.17	7.47	19.45	20.40	0.55
5tons/ha Pig dropping	33.58	7.22	15.33	15.14	0.53
10 tons/ha Pig dropping	33.17	7.15	14.16	5.74	0.53
Zero manure application	33.08	6.41	12.72	3.96	0.40
	ns	ns	ns	ns	ns

NF = Number of fruit, FL = Fruit length, FD= fruit diameter, FW= fruit weight

Discussion

Statistical analysis indicated that number of branches of cucumber was significantly affected by the different rate of application of goat and pig droppings. In terms of yield, Goat droppings at 5 tonne per hectare performed best in most growth parameters followed by 10 tons/ha of pig droppings, although there was no significant different in terms of yield but however yield parameters had best performance from 5 tons/ha of goat manure, This result is contrary to the findings of Chiezey and Odunje (2009) who observed that application of organic manure gives significant improvement in crop growth and yield.

Soil analysis of pre-data and post planting of the experimental site

The physiological properties of the experimental soil were presented in table 6. It was shown that the soil was sandy clay loam in texture, with high portion of sand (70.5%). This implies that basic cation such as Ca, k, Na and Mg could be leached more easily as texture determines the degree of retention or ease of leaching of basic cations according to Wapa and Oyetayo, 2014.

The pre-soil analysis shows that pH was 5.51, while in the post soil analysis the soil was slightly acidic which varied from 5.15-6.13 for the treated plots. The soil pH for the control was 5.49. Soil treated with pig droppings at 10 tons/ha had the least pH value of 5.15 while plot treated with goat droppings at 5tons/ha had the highest value of 6.13. Soil acidity has been reported as one of the major constraints to crop growth in tropical region. This implies that organic manures could serve as good materials for ameliorating acidic soil to 6-7 as reported by Sanni.and Adenubi, (2015) that pH requirement for optimum growth and yield of eggplant being pH 6.4.

The pre-soil analysis revealed that the soil was low in organic carbon (0.42%), organic matter (0.72%), total N (0.04%), Ca (3.79cmol/kg) available p was higher (34.80mg/kg), but increased in the post-soil analysis. Organic carbon for control was 1.7%, it varied between 1.30%-2.03% for treated plots, and plot treated with goat droppings at 5tons / ha had the highest value of 2.03% while the lowest value (1.30%) was observed from soil treated with pig dropping at 5tons /ha.Total N for control was 0.15%, it varied between 0.11-0.18 for treated plot, plot treated with goat droppings at 5 tons/ha had the highest value (0.18%) while the least value (0.11%) was observed from soil treated with pig droppings at 5tons/ha.

Available p for control plot was 10.61 mg/kg, it varied between 9.57-21.05 for treated plot, goat droppings at 5 tons/ha had the highest value of 21.05mg/kg while the least value(9.57mg/kg) was observed from plot treated with pig droppings at 5tons/ha.

Exchangeable Ca for control was 6.76 cmol/kg) while plot treated with goat droppings at 5tons/ha had the highest value with 7.96 and plot treated with pig droppings at 10 tons/ha had lowest value of 5.67cmol/kg.

Table 4.5. *Soil properties at experimental site and soil physio-chemical as influenced* *manure*

Sample label	Pre field trial soil analysis	Post field trial soil analysis				
		Goat 5t/ha	**Goat10t/ha**	**Pig 5t/ha**	**Pig10t/ha**	**Control (0t/ha ha)**
pH(H20)	5.51	6.13	5.35	5.57	5.15	5.49
O.C (%)	0.42	2.03	1.84	1.30	1.44	1.76
O.M (%)	0.72	3.51	3.16	2.34	2.48	3.03
TN (%)	0.04	0.18	0.16	0.11	0.12	0.15
Na (Cmol/kg)	0.131	8.09	8.21	7.96	7.96	8.35
Ca (Cmol/kg)	3.79	7.96	5.67	6.39	7.10	6.76
Mg (Cmol/kg)	0.67	2.95	2.39	2.37	2.74	3.13
K (Cmol/kg)	0.10	3.15	5.37	3.15	3.53	3.84
H (Cmol/kg)	1	1	1.5	2	1	1
AL (Cmol/kg)	0.4	0.3	0.2	0.3	0.1	0.2
CEC (Cmol/kg)		23.34	23.34	22.17	22.82	23.41
Fe (mg/kg)	44	133.7	103.7	124.9	133.7	138.2
Cu (mg/kg)	1.8	20.11	3.73	3.16	3.68	5.45
Mn (mg/kg)	41.8	246	276	164	440	480
Zn (mg/kg)	4.9	30.02	31.52	21.10	44.16	49.72
P (mg/kg)	34.8	21.05	15.14	9.57	20.71	10.61
% Sand	70.5	72.5	72.5	72.5	74.5	74.5
% Clay	21	21	21	21	19	19
% Silt	8.5	6.5	6.5	6.5	6.5	6.5
TC	SCL	SCL	SCL	SCL	SL	SL

treatment

Source: Forestry research institute of Nigeria, Ibadan
Soil and tree nutrition department

However, Akinrinde and Obigbesan, (2000) recommended appropriate organic carbon, organic matter, TN, Ca, Available P for sustainable crop production in agro-ecological zones of Nigeria as these components (OC, OM, TN, Ca, and P) are important nutrients required for plant growth, development and yield formation. Therefore, the soil requires amendment from different sources of nutrients to ameliorate their deficiencies and responses to organic manure applied was highly anticipated.

The pre-soil analysis shows that Fe (44mg/kg), Cu (1.8mg/kg), Mn (41.8mg/kg), Mg (0.67Cmol/kg), k (0.10Cmol/kg) and Zn (4.9mg/kg) were low, meanwhile they were far more higher in post field trial soil analysis. Abdul-Allah *et al*. (2001); Boyoumi, (2005) and Ehaliotis *et al*. (2005) had reported that Fe, Zn, and Mn encourages vegetative growth, total chlorophyll and the photosynthetic rate of plants which enhance flowering and fruiting thus leading to an increase early maturity. More so, Abou-Hussein (2001) reported that cucumber fruit made used of more K and Mg than major nutrients in the soil which helps in increasing fruit sets, encourage root growth, promotes leaf growth and reduces plant respiration.

Exchangeable H was 1Cmol/kg in the pre-soil analysis while it was observed in the post soil analysis that the control plot, plot treated with 10 tonnes/ha of pig droppings and plot treated with 5 tonnes/ha of goat droppings had same value of 1Cmol/kg with the pre-soil analysis, which was also observed has the lowest values while the highest value was obtained from plot treated with 5 tonnes/ha of pig droppings. Exchangeable Al was high (0.4Cmol) in the pre-soil analysis but low in post-data analysis, it varies from 0.1-0.3 for treated plot while control plot was 0.2 Cmol/kg. However, Aluminum toxicity is potential growth-limiting factor of plant grown in acid soil worldwide. Acid soils (with a pH of 5.55 or lower) are most prone to aluminium toxicity to limit agricultural production. The total Al concentration in the soil and the forms of Al species depends on soil pH and the chemical environment of the soil solution (Kisnierinene and Lepeikaite, 2015).

The pre-soil analysis shows that sand, clay, silt are 70.5%, 21% and 8.5% respectively meanwhile post-data analysis revealed that plot treated with goat at 5tons/ha , goat at 10tons/ha followed by pig at 5tons/ha had same value of sand, clay, silt with 72%, 21%, 6.5% and same textural class(SCL) respectively, similarly plot treated with pig at 1otons/ha and plot without treatment(control 0ton/ha) had same percentage of sand (74%), clay(19%), silt(6.5%) and same textural class(SL)respectively. Control has CEC of 23.41 which was improved in plot treated with goat droppings at 5 ton/ha with value 23.45 This implies that basic cation such as Ca, k, Na and Mg would be leached more easily as texture determines the degree of retention or ease of leaching of basic cations (Wapa and Oyetayo, 2014)

Conclusion

In terms of growth parameters 5 and 10 tonnes per hectare goat droppings had the best performance even if there was no significant difference but however, in terms of yield 5 tonnes per hectare of goat droppings had a better performance

Recommendation

Based on the outcome of the study, 5 tonnes of goat droppings per hectare should actually be adopted for farmers in Ikorodu Local Government Area of Lagos State.

However, further research should be carried out to determine the rate of manure suitable for the optimum yield of cucumber (*Cucumis sativus)*. Farmers are advised to used more tones of manure at a higher rate to improve soil physio-chemical properties and to enhance crop growth and yield.

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Groundwater Quality Dynamics from Field Experiments on Watershed Level in Southern Bulgaria.

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Abstract

The results of the groundwater dynamics are presented realized on the territory of a small watershed at the experimental station Tsalapitsa in South Bulgaria, under Fluvisol. The shallow waters of three permanent built wells from the experimental field were studied when growing different crops with different fertilization for the period 2016-2018. The samples for chemical analysis were taken monthly. It was found that different agricultural practices influenced significantly on the content and dynamics on nitrogen in the shallow groundwater. The highest concentration of nitrogen were measured when vegetables were grown, while at a change in the loading with fertilizers the values are lower around and below MPCL The calcium concentrations of groundwater vary in considerably short range, such as correlates to a certain extent with the nitrate content.

Key words: groundwater, chemical composition, agriculture, fertilization

Introduction

Groundwater is one of the most valuable water resources**.** It is known that the protection of groundwater quality is actual problem not only for economic reasons, but also because of its great social significance. The conducted researches (Beaudoin et al., 2005; Stoicheva et al., 2013; Simeonova et al., 2015, 2017; Singh et al., 2018; Wang et al., 2013) in recent showed a significant load of surface and underground water with nitrogen and other nutrients in areas with iimproper fertilization, livestock farms and urban areas. The chemical composition of groundwater depends on natural factors (soil, geology, climate) and anthropogenic impact (fertilizers, irrigation, etc). Groundwater protection is of particular importance, as hydrological indicators show that water quality is slowly improving after changes in agricultural practice. It is known that studying of pathways and mechanisms for nutrients leaching out of the root zone and their downward movement through the intermediate vadose zone on a watersched level is a very difficult task, because of the hidden and complicated character of the processes. Acording to some authors the use of modeling approaches to study groundwater pollution or the interaction between surface water and groundwater has become a trend, but the accuracy of the modeling results greatly depends on the accuracy of the information and on the magnitude and distribution of aquifer permeability (Sanford, 2002; Piccini et al., 2016). The EU focuses on sustainable and environmentally sound farming, by developing a thematic strategy on soil (European Commission, 2006 a, b) and water protection (Directive 91/676/EEC and Directive 2000/60/EEC).

The aim of this study is to present results on monitoring the dynamics of chemical elements in the shallow groundwater in a field experimental station on Fluvisol under conditions of changing anthropogenic loading.

Material and Methods

The field experiment is located in south Bulgaria (24035’E; 42014’N), near the city of Plovdiv in the village of Tsalapitsa. The region belongs to the transition subzone between Moderate and Mediterranean Continental climate zones. According to the classification of the country thermal conditions, the experimental area belongs to temperate hot and dry zone Levichanska (1991). The region is characterized with mean annual climatic data on: annual precipitation of 340 mm in 2016; 494,5 mm in 2017; and 482 mm in 2018. The average rainfall for this region of 500-540 mm.The average annual air temperature is 12.5-12.8 ^{0}C. The soil was classified as Alluvial-meadow soil Koynov (1987), which corresponds to Eutric Fluvisol in FAO classification (FAO, WRBSR, 2015). The hydrogeological research on the territory shows high spatial heterogeneity of the thickness and distribution of the alluvial materials (Stoichev et al., 1980; Mateva et al., 1982). The sandy clay loam soil has AC type of profile and a high infiltration rate and permeability.The depth of groundwater level varies between 2.6 and 4.8 m. (during the period of research varied to 5.9 m) The soil profile has coarse texture, low water holding capacity and conditions for fast water movement downward the profile, which is a precondition for migration of the dissolved materials through the soil profile. The arable horizon has the following mean characteristics: light texture, low clay content, bulk density between 1.54 and 1.66 g.cm^{-3}, pH$_{H2O}$ is 6.0 – 6.5, low humus and total nitrogen content, respectively 0.70% and 0.052 %, low cation exchange capacity in the plough soil layer total. The physico-chemical properties of the soil are presented in Table 1. Fluctuation of the shallow groundwater table was monitored at three (№ 5, 6, 7) permanent wells (∅ 220 mm) and samples for chemical analysis were taken monthly. The assessment of groundwater chemical composition was based on data for the period of 2016-2018, where different agricultural crops were grown which are fertilized with different N-rates on the background of the phosphorus and potassium. The pH values and chemical elements (K^+, Na^+, Ca^{2+}, NO_3^-, HCO_3^-, Cl^-, $SO^4{}_2{}^-$) of groundwater samples are determined using the laboratory methods of analysis described in Arinushkina (1970) and Page et al., (1982).

Table 1. *Characteristics of the studied Fluvisol*

Horizons	Depth, cm	pH$_{H2O}$	Humus %	Total N, %	C:N	CaCO$_3$, %	Sorption capacity, meq.100g^{-1}	Particle size, mm 2.0-0.02 %	0.02-0.002 %	< 0.002 %
				Alluvial-meadow soil - Fluvisol						
A$_{arable}$	0-35	6.0	0.70	0.052	7.8	0.00	7.92	66.3	16.2	17.5
A$_2$	35-60	6.4	0.55	0.050	6.4	0.00	18.18	43.4	14.8	41.8
A$_3$C$_1$	60-87	6.5	0.42	0.042	5.8	0.00	22.77	33.5	20.6	45,9
C$_2$	87-118	6.5	0.38	0.030	7.5	0.00	23.11	31.4	29.6	39.0

According to D.Stoichev, 1997.

Results and Discussion

Data on groundwater table fluctuation during the monitoring period are presented in Table 2. The dynamics of the groundwater table detected during the monitoring period follows the seasonal distribution of the precipitation. The variation of the average amount of precipitation during the studied period reach to 100 mm. The data show that spring-summer and autumn maximums of precipitation were observed.

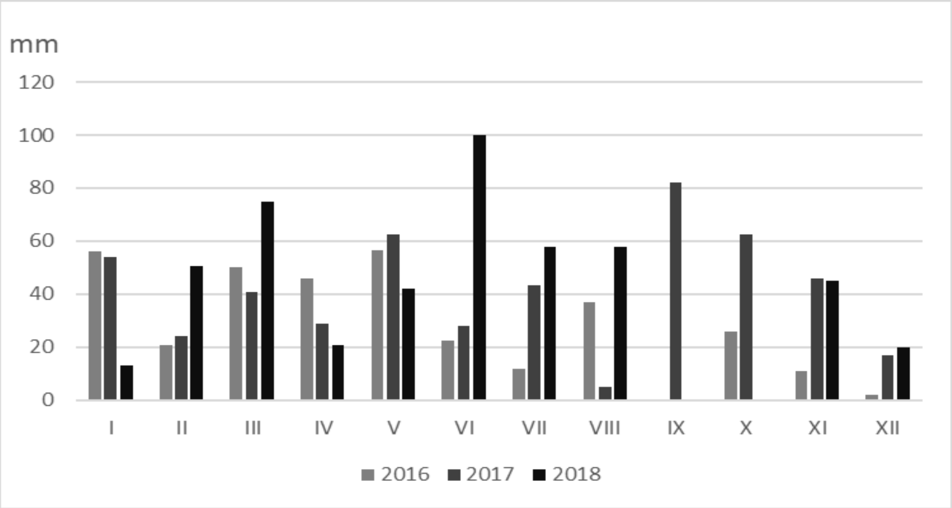

Fig. 1. *Monthly precipitation sums for the periods 2016-2018 in Tsalapitsa, South Bulgaria.*

The highest water table fluctuation was observed in monitoring well №6 during the whole studied period.

Table 2. *Depth of groundwater table (wells № 5,6,7) in the experimental field Tsalapitsa, the period (2016-2018).*

No of wells			
Depth,m	**5**	**6**	**7**
Min	4.4	4.7	4.0
Max	5.6	5.9	5.0
Mean ±Stdv	5.07±0.25	5.28±0.29	4.53±0.20

The groundwater samples obtained from the three monitoring wells have neutral to alkaline reaction throughout the study period (Figure 2). Fluctuation of the pH values in the three wells is almost the same. Two deviations were observed, one in March 2016 when the pH in well № 5 (pH 6.9) was the lowest compared to the other wells and the other in November 2020, when the measured pH 8,60 in well № 6 was higher than in the other two wells. These differences are statistically not significant. No seasonality was found on the pH values .

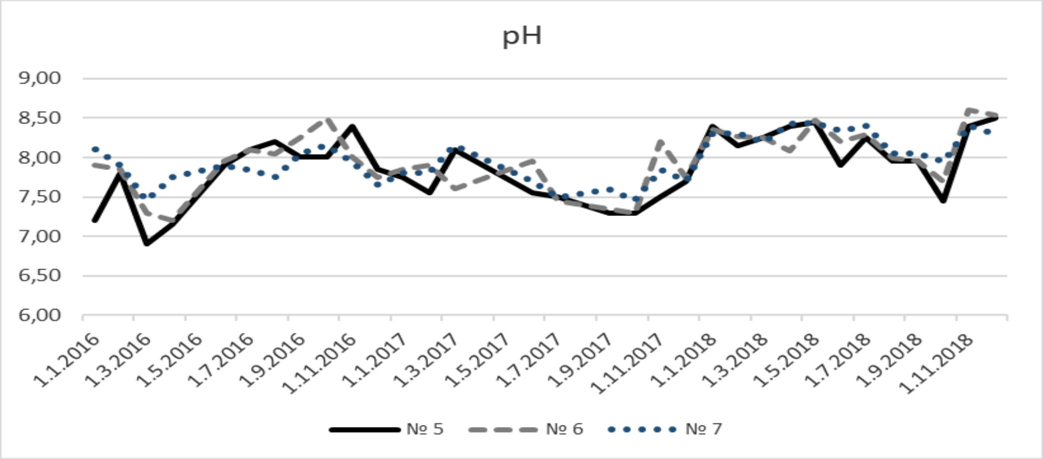

Fig. 2. *pH of groundwater in the experimental field Tsalapitsa, during the period (2016-2018).*

Table 3. *Chemical composition (mg.l^{-1}) of the studied wells in the experimental field Tsalapitsa during the period (2016-2018).*

	No of wells		
Elements, mg.l-1	**5**	**6**	**7**
K+			
Min	0.22	0.33	0.16
Max	1.68	5.01	2.01
Mean ±Stdv	0.83±0.39	1.42±0.43	0.82±0.48
Na+			
Min	25.72	22.98	19.63
Max	45.00	50.78	41.64
Mean ±Stdv	31.76±5.15	29.37±6.08	26.79±4.83
Ca2+			
Min	32.50	29.50	28.00
Max	93.40	91.50	77.50
Mean ±Stdv	69.82±17.23	64.9±16.09	56.83±12.88
NO3-			
Min	12.73	10.43	4.40
Max	68.70	43.20	34.40
Mean ±Stdv	35.71±13.42	26.2±6.81	17.89±7.32
HCO3-			
Min	172.08	190.00	198.62
Max	358.04	414.38	358.05
Mean± Stdv	307.95±36.65	270.83±42.26	299.20±36.02
Cl-			
Min	6.13	5.00	6.70
Max	15.10	21.00	13.90
Mean ±Stdv	10.66±2.19	13.79±3.06	10.00±1.98
SO42-			
Min	79.00	67.00	58.00
Max	140.00	150.00	122.00
Mean ±Stdv	104.6±15.23	95.63±18.47	89.97±18.26

On Figure 3, the dynamics in the K^+ content in the groundwater is presented. In general, potassium is an element, which is characterized with very low mobility coefficient. It is subject to physico-chemical fixation.

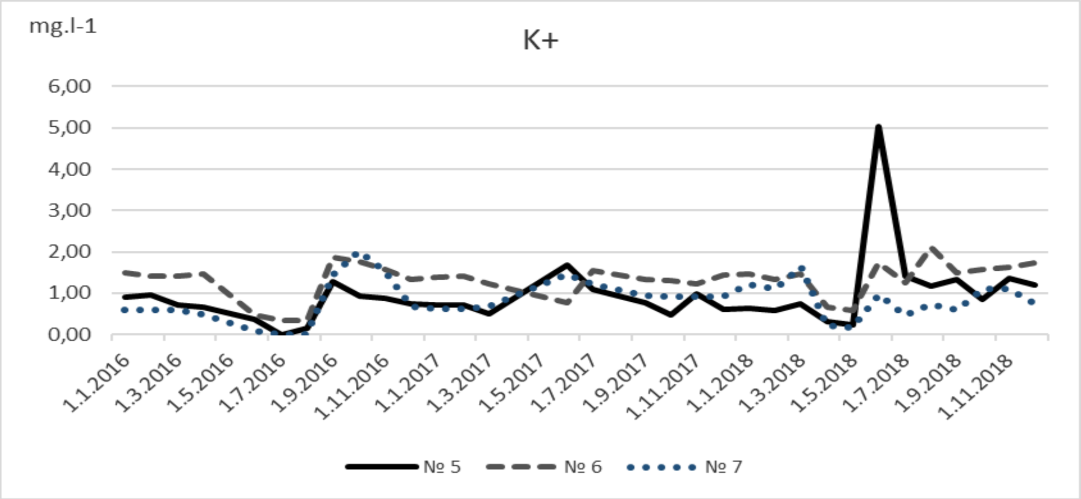

Fig. 3. *Dynamic of potassium content in groundwater in the experimental field Tsalapitsa, during the period (2016-2018).*

The highest of K+ content was observed in the well № 6, which is close to the long-term fertilizer experiment. Potassium content varies from 0.16 to 5.02 mg.l-1 (Table 3), while the lowest values was measured in the summer months of 2016 and the spring months of 2018 at all three wells.

The dynamics of sodium in groundwater (Figure 4) from all studied wells follows almost the same trend of changes over time. Sodium as compared to potassium has higher values in the groundwater (19.63-50.78 mg.l-^{1}). Sodium is an element with high geochemical mobility and transitional status in the geochemical cycle and due to this reason it is highly influenced by the changing anthropogenic loads. (change in fertilizer rates, reduced water available to move around the profile, and cultivated crops (cereals without irrigation).

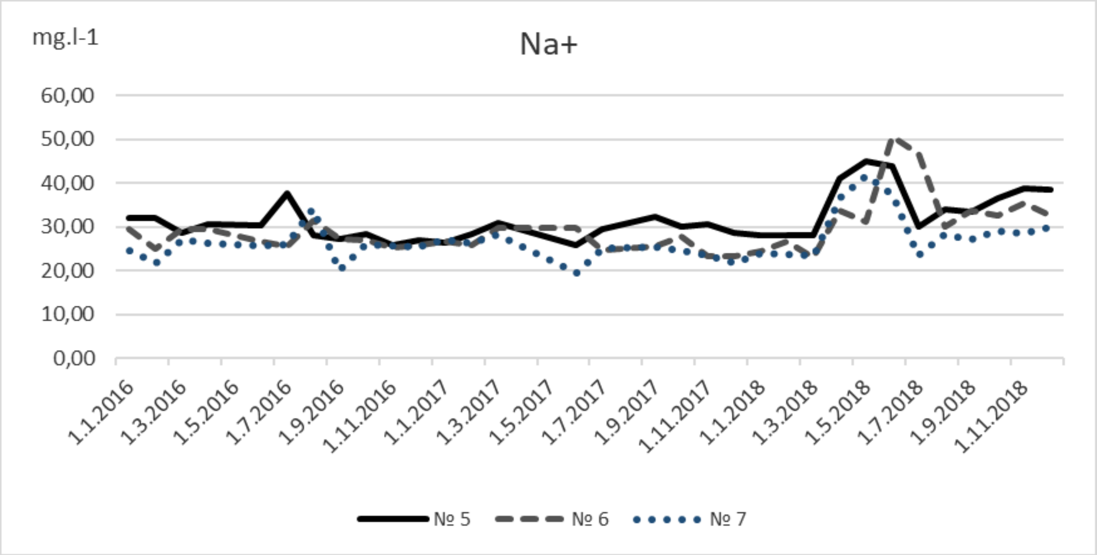

Fig. 4. *Dynamic of sodium content in groundwater in the experimental field Tsalapitsa, during the period (2016-2018).*

As it is shown on Table 3, calcium concentrations in groundwater varies from 28.0 to 93.4 mg.l^{-1}, which is not typical for this element due to its high mobility and status in the geochemical cycle of elements. Similar behavior of calcium was found in a study by Stoicheva et al., (2013).

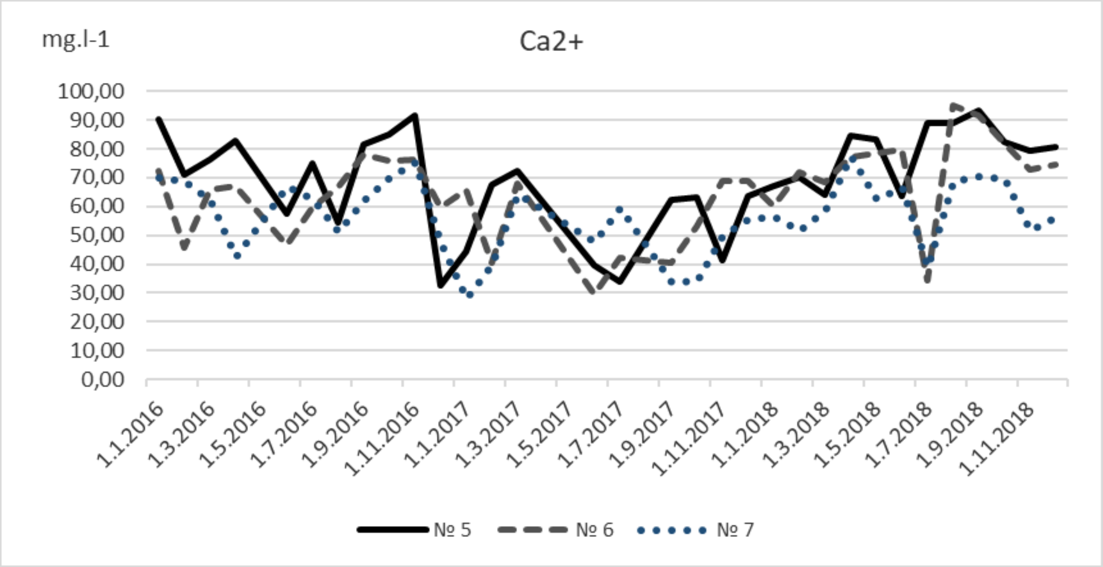

Fig. 5. *Dynamic of calcium in groundwater in the experimental field Tsalapitsa, during the period (2016-2018).*

Although the variation is not so big, its temporal pattern seems to follow that of the nitrate content. Calcium concentrations for the study period did not exceed the MPCL for drinking water (150 mg.l^{-1}).

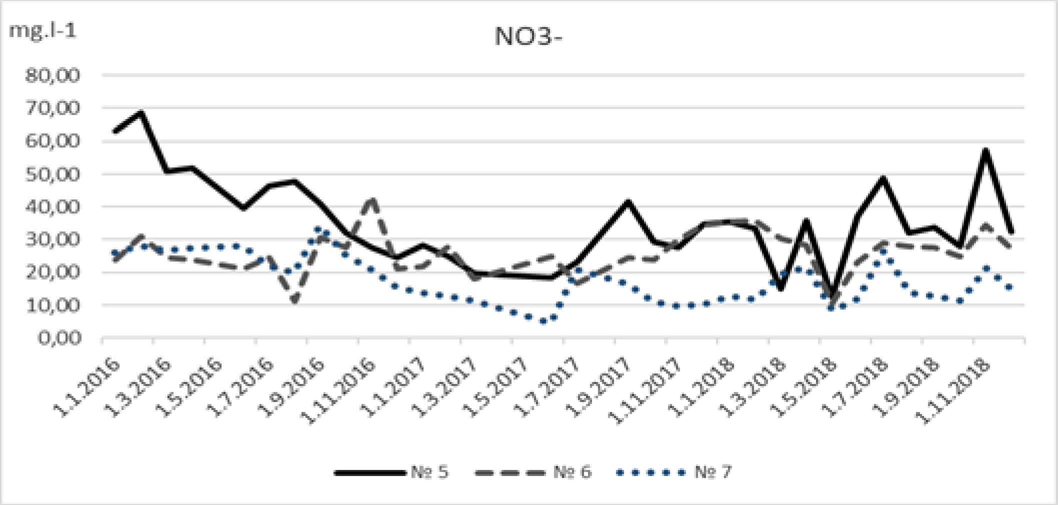

Fig. 6. *Dynamic of nitrate content in groundwater in the experimental field Tsalapitsa, during the period (2016-2018).*

In their study Li P et al., (2013 a,b) found that, mineral weathering (carbonate and silicate minerals) and ion exchange are the most important factors controlling groundwater chemistry. Nitrogen distriburion assessment on a watershed level is usually difficult because of lack of information for the vadose zone, the uncertainties of nitrogen input and soil and landscape diversity. Data on nitrate content for the periods 2016-2018 (Figure 6) confirm the tendency of decreasing nitrate concentration compared to previous study periods in the experimental field Stoicheva et al., (2013). Tne average values of nitrates around and below the maximum permitted contamination are observed. But there are peak values of nitrate during spring-autumn months. The highest concentrations of nitrate in monitoring wells N5 were registered in February 2016 and November 2018.

Fluctuation in the nitrate concentrations varied in a range of 20-45 mg.l^{-1}. However, the absolute values in the three wells were different. The lowest nitrate concentration – 4.40 mg.l^{-1} in average was measured in the samples taken from monitoring well № 7 and the highest – 68.70 mg.l^{-1} in average in well № 5.

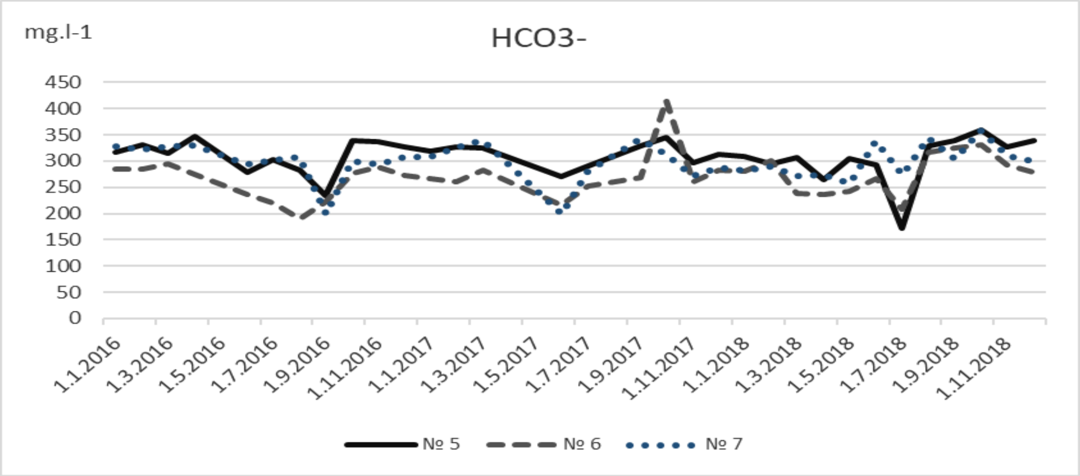

Fig. 7. *Dynamic of hydro-carbonates content in groundwater in the experimental field Tsalapitsa, during the period (2016-2018).*

The coefficient of variation reaches to 45 % (at $p \leq 0.05$), the highest being in well 7. The coefficient of variation is similar for potassium also in well 7 which indicates that the variation in these elements under this particular soil have one and the same origin.

The concentrations of hydro-carbonates range from 172.08 to 414.38 mg.l^{-1} was detected (Figure 7), such as the highest values are found in well № 6. The data do not show any spatial or temporal dependence from other measured concentrations. Chlorine content in the groundwater could be characterised with considerably low variation in space and time. (Figure 7). His behavior is almost the same as for calcium concentrations. The data have a narrow range (5.0-21.0 mg,l^{-1}), which is not typical for this element due to its high mobility and in the geochemical cycle.

The highest Cl content was observed in May 2018. The anthropogenic loads strengthened the dynamics of chlorine in groundwater because of the absence of mechanisms in the soil to adsorb chlorine from drainage water. Chlorine, like sodium, has a transitional status in the biological turnover of nutrients. The data show (Table 3), that the sulfates concentrations vary from 58.0 to 150 mg.l^{-1}, with the highest values are found in the well n 6.

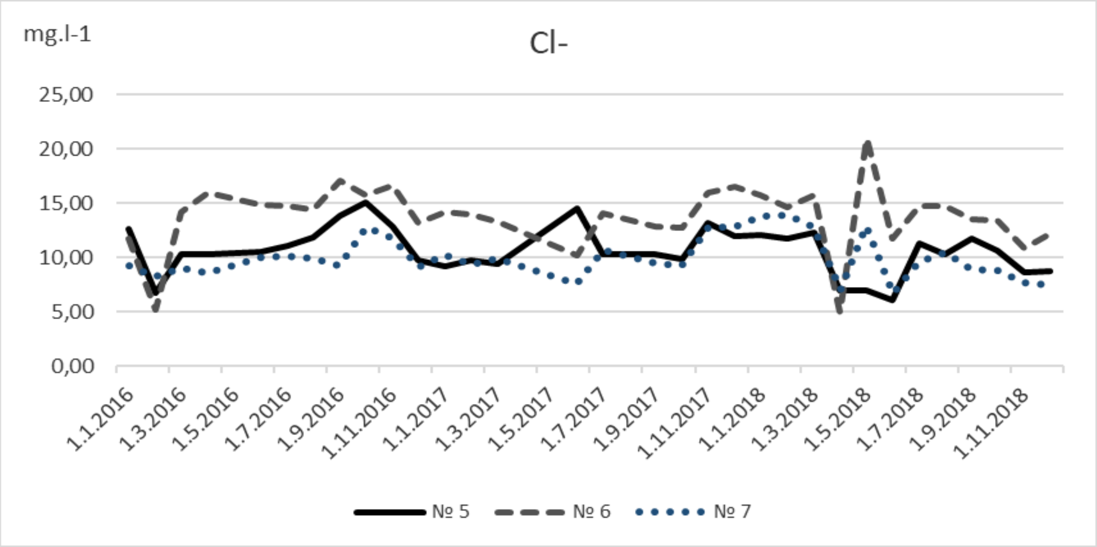

Fig. 8. *Dynamic of chlorine content in groundwater in the experimental field Tsalapitsa, during the period (2016-2018).*

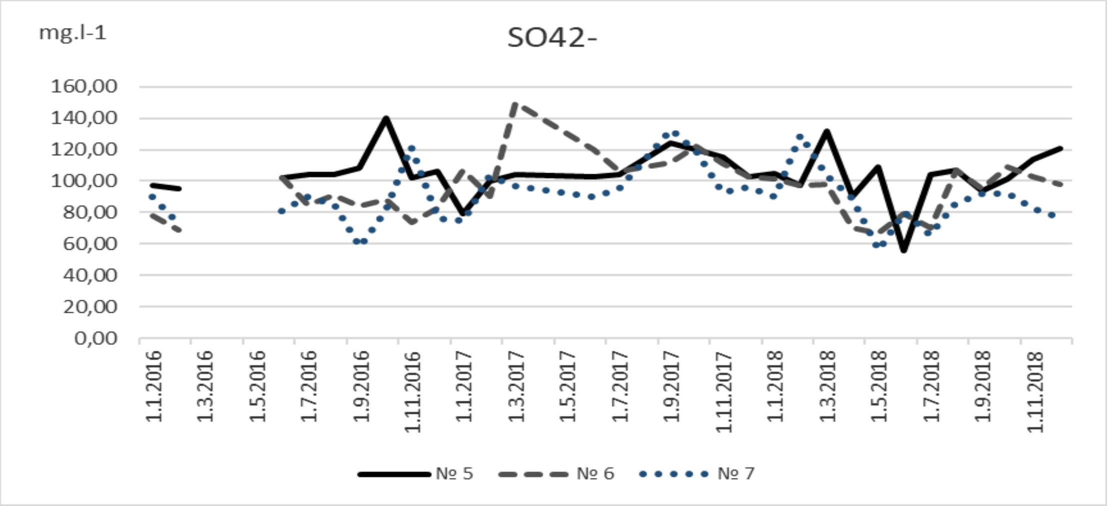

Fig. 9. *Dynamic of sulphates content in groundwater in the experimental field Tsalapitsa, Plovdiv region during the period (2016-2018).*

Conclusion

It was established that groundwater samples in the studied watershed has neutral to alkaline reaction and hydrocarbonate-calcium composition. It was found that fluctuations in the three wells levels are similar. Correlation between the dynamics of potassium and nitrate contents was recognized which indicate that temporal fluctuation should have the same origin. The calcium concentrations in groundwater do not exceed the maximum permissible contaminate level for drinking water and its fluctuation corresponds to that of the nitrate content. Nitrate content in the groundwater was influenced by the anthropogenic loads and a decreasing trend in nitrate concentration was observed when fertilization is reduced. It was monitored a significant variation in the data for hydro-carbonates content in the groundwater, slightly influenced by the anthropogenic loading. Chlorine and sulphate contents in the groundwater could be characterised with lower variation. A similar coefficient of variation was found for both elements respectively (Cv= 14 to 22 % at $p \leq 0.05$).

As a general conclusion, the intensive agricultural activity of alluvial-meadow soil creates conditions for more dynamic water movement through the soil profile and migration of some chemical elements.

Acknowledgement

This work was supported by the Bulgarian Ministry of Education and Science under the National Research Programme "Protecting the environment and reducing the risk of adverse events and natural disasters" - 1.3. "Quality of national water resources (surface and groundwater)" approved by DCM # 577 / 17.08.2018".

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Example: **Table 1.** *Soil indexes of the territory (2015–2016).*

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Example: **Fig. 1.** *Soil map of the study area.*

Citation and References

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Journal articles

- Atanassova, I., Doerr S. (2010). Organic compounds of different extractability in total solvent extracts from soils of contrasting water repellency. *European Journal of Soil Science*, 61(1),298-313.
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